

Chemical Monographs

# FIXATION OF ATMOSPHERIC NITROGEN

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JOSEPH KNOX



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# CHEMICAL MONOGRAPHS

EDITED BY A. C. CUMMING, O.B.E., D.Sc., F.I.C.

No. IV

The Fixation of Atmospheric Nitrogen

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THE progress of Chemistry is so rapid that it is becoming a matter of ever-increasing difficulty to keep abreast of the modern developments of the science. The volume of periodical literature is so enormous that few can hope to read, far less assimilate, all that is published. The preparation of summaries has therefore become a necessity, and has led to the publication of various well-known journals devoted to the abstraction of original papers. For obvious reasons, however, these do not fully supply the wants of advanced students and research workers, and it is now generally recognised that monographs on special subjects are also needed.

This series of monographs is intended primarily for Advanced and Honours students. As each monograph is written by an author with special knowledge of the subject, and copious references are given, it is hoped that the series will prove useful also to those engaged in research.

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# The Fixation of Atmospheric Nitrogen

BY

JOSEPH KNOX, D.Sc.

*Lecturer on Chemistry, University of Glasgow*

SECOND EDITION

NEW YORK

D. VAN NOSTRAND COMPANY

EIGHT WARREN STREET

1921

75202



## PREFACE

IN the following pages I have tried to give an account of the more important processes for the fixation of atmospheric nitrogen, and, more especially, of the theory on which they are based. No attempt has been made even to mention all the proposals regarding methods and apparatus to be found in the patent literature of recent years. The mere enumeration of these would almost occupy the space at my disposal, and in many cases there is no evidence that the proposed methods are in any way workable. I have, therefore, confined myself to those methods which are either in actual operation, or which show promise of assuming technical importance in the near future. I am indebted to the admirable consular report on *The Utilisation of Atmospheric Nitrogen*, by T. E. Norton, for some valuable information on the purely technical part of the subject. The report also contains an excellent account of the financial and commercial organisation of the various industries connected with the fixation of nitrogen.

J. K.

ABERDEEN, *April* 1914.

## PREFACE TO SECOND EDITION

COMPARATIVELY little work of importance on the theoretical side of nitrogen fixation has appeared since the first edition of this book was published. On the other hand, the development of fixation processes on the technical side received an enormous impulse under the stress of war conditions. The chief progress has been in the production of synthetic ammonia by the Haber and cyanamide processes, and in the methods of oxidising ammonia to nitric acid. The expansion in the production of synthetic nitrogen compounds has been remarkable. The estimated production of the various nitrogenous compounds for 1917, in short tons of nitrogen, is given as follows by the American Ordnance Department:—

Chilean nitrate	. 382,000	short tons of nitrogen	
By-product ammonia	461,000	”	”
Calcium cyanamide	168,000	”	”
Arc process	. 34,000	”	”
Haber process	. 114,000	”	”

In this short summary no attempt has been made to go into the question of the relative cost of the nitrogen compounds produced by the various processes. This question is fully covered, so far as data are available, by the invaluable “Final Report of the Nitrogen Products Committee of the Ministry of Munitions of War,” published in 1920 by H.M. Stationery Office.

J. K.

GLASGOW, *March* 1921.

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# The Fixation of Atmospheric Nitrogen

## INTRODUCTION.

UNTIL a few years ago, practically the only sources of inorganic nitrogen compounds were the sodium nitrate deposits of Chile, and the ammonium compounds obtained in the destructive distillation of coal. These sources supplied the raw material for the manufacture of the enormous quantities of nitric acid and ammonia used in the chemical industries. In addition, both sodium nitrate and ammonium sulphate are used as manures to supply the nitrogen necessary for plant growth. The great majority of plants are unable to assimilate nitrogen in the free form in which it occurs in the atmosphere, but take it up from the soil in the form of nitrates. During the slow decay of organic nitrogenous manures, the nitrogen is first converted into ammonium compounds, which are then transformed into nitrates by the nitrifying bacteria in the soil. The nitrogen in ammonium sulphate undergoes a similar transformation before its absorp-

tion by plants. Short accounts of the circulation of nitrogen in nature and its absorption by plants are given by v. Braun,<sup>1</sup> Stewart,<sup>2</sup> and Crossley.<sup>3</sup> Owing to the intensive cultivation of food crops necessitated by the steadily increasing population of the world and the growing demand for a higher standard of living in all civilised countries, the natural supply of nitrates to the soil has to be augmented by the application of artificial nitrogenous manures, chiefly sodium nitrate and ammonium sulphate, and the consumption of these substances for manurial purposes has increased enormously since their introduction, and is steadily increasing. An excellent account of the Chile saltpetre industry, with relative statistics, is given by Norton,<sup>4</sup> and by Hobsbaum and Grigioni.<sup>154</sup> The export of nitrate from Chile rose rapidly from 935 tons in 1830 to 2,770,000 tons in 1914. The South American deposits contain enormous, but not unlimited, quantities of nitrate. The earlier alarmist estimates of their probable life<sup>5</sup> have, as a result of recent surveys and new discoveries, proved erroneous. The official Chilean estimate<sup>154</sup> is 200 years, which, with improved methods of working and the tapping of lower grade deposits, may be probably at least doubled. In spite of this, the lessons of the four years of war should alone be sufficient to stimulate interest in the production of synthetic nitrates in this country, and the efforts to establish such an industry should receive every encouragement from the State, which is vitally interested in the matter.

The total production of by-product ammonia and

ammonium compounds, the chief source of which is the nitrogen in coal, increased greatly during the war, and the amount of fixed nitrogen in this form was estimated in 1917 to exceed the fixed nitrogen contained in the world's consumption of Chile saltpetre. In 1913 the world's production of by-product ammonia, calculated as ammonium sulphate, was about 1,400,000 tons, and Britain's share was 432,000 tons. In 1917 the estimated world's production was about 2,000,000 tons and Britain's share about 470,000 tons.

In the event of the cutting-off of the Chilean supplies from Britain, especially in war time, the production of by-product ammonia would not be sufficient to cover the demands of the chemical industries and of agriculture. As a further incentive to the development of processes for the fixation of nitrogen there is the probability that synthetic nitrogen compounds, such as nitric acid and ammonia, will be able to compete economically with Chilean nitrate and by-product ammonia.

In the atmosphere, which consists approximately of 21 per cent. oxygen and 79 per cent. nitrogen by volume, there is an inexhaustible store of nitrogen. It has been calculated that the atmosphere contains about 4,000,000,000,000,000 tons of nitrogen, or that in the air over every square mile of the earth's surface there are about 20,000,000 tons. In recent years an enormous amount of work has been done on the conversion of atmospheric nitrogen into technically important nitrogen compounds, especially into nitrates and

ammonium compounds, since these are the forms of combined nitrogen for which both the chemical industries and agriculture make the largest demand.

In what follows we shall consider the more important attempts which have been made to utilise atmospheric nitrogen, and we may classify the methods employed under three main headings:—

(1) Conversion of nitrogen into nitric or nitrous acids and their salts.

(2) Synthesis of ammonia and ammonium compounds from atmospheric nitrogen.

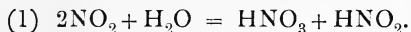
(3) Conversion of atmospheric nitrogen into compounds which readily yield ammonia.



## SECTION I.

### FIXATION OF ATMOSPHERIC NITROGEN AS NITRIC AND NITROUS ACIDS OR AS THEIR SALTS.

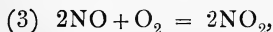
**Summary of Process.**—The first step in the fixation of atmospheric nitrogen as nitric or nitrous acids or their salts consists in oxidising the nitrogen to nitric oxide. The air itself contains the necessary oxygen, so that in the atmosphere we have an unlimited supply of the requisite raw materials. The NO is then further oxidised by excess of atmospheric oxygen to  $\text{NO}_2$ , and the  $\text{NO}_2$  may be converted into nitrate or nitrite by choosing the proper conditions of absorption. When the  $\text{NO}_2$  is absorbed by water, a mixture of nitric and nitrous acids is first produced.



Free nitrous acid is, however, unstable under ordinary conditions and decomposes as follows :—

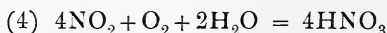


In presence of excess of oxygen the liberated NO is oxidised to  $\text{NO}_2$ ,



which, in contact with water, goes through the same

series of reactions, until practically the whole of the original  $\text{NO}_2$  is converted into nitric acid. By multiplying equation (1) by 3 and adding the result to equations (2) and (3) we obtain

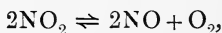


as the total equation representing the oxidation of  $\text{NO}_2$  to nitric acid. The reaction represented by equation (4) is complete, however, only when excess of water is used, so that it is not possible to prepare concentrated nitric acid by this means.

The absorption of  $\text{NO}_2$  by alkalis under ordinary conditions of temperature and pressure takes place essentially according to the equation—



and results in the formation of equivalent quantities of nitrate and nitrite. Nitrogen peroxide, however, begins to dissociate above  $140^\circ \text{C.}$  according to the equation—



and the degree of dissociation increases with increasing temperature, until at about  $620^\circ \text{C.}$  the dissociation is complete. Now a mixture of equimolecular proportions of  $\text{NO}$  and  $\text{NO}_2$  behaves towards alkali as nitrous anhydride,  $\text{N}_2\text{O}_3$ , and on absorption produces practically pure nitrite,



The gas obtained by the oxidation of atmospheric nitrogen therefore consists, between  $140^\circ$  and  $620^\circ$ ,

of a mixture of  $\text{NO}$ ,  $\text{NO}_2$ , and air, the proportions depending on the temperature. By choosing the proper temperature it is, therefore, possible to obtain practically pure nitrite by absorbing the gas-mixture with alkali.

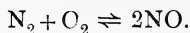
**The thermal equilibrium between nitrogen, oxygen, and nitric oxide.**—That nitric oxide or its oxidation products, nitrous and nitric acids, could be obtained by the direct union of nitrogen and oxygen at high temperatures has long been known. Thus by sparking a mixture of nitrogen and oxygen in presence of water or caustic potash, Cavendish obtained nitric acid or potassium nitrate. By the combustion of hydrogen and various other substances in a mixture of nitrogen and oxygen, nitrites and nitrates are also produced. A very complete bibliography of the older literature on the subject is given in Gmelin-Kraut.<sup>6</sup>

On the other hand, the decomposition of nitric oxide into nitrogen and nitrogen dioxide by electric sparks had been observed by Priestley, and numerous investigators<sup>7</sup> subsequently studied its decomposition by heat or by the electric spark or arc. The results of these investigations, especially as regards the temperature at which decomposition becomes appreciable and the extent of the decomposition at different temperatures, are very conflicting.

It was gradually recognised that the primary product of the interaction of nitrogen and oxygen at high temperatures was nitric oxide, and that in the decomposition of nitric oxide by heat the primary products are nitrogen and oxygen. The occurrence

of higher oxides of nitrogen, such as  $\text{NO}_2$ , or, in presence of water, of  $\text{HNO}_2$  and  $\text{HNO}_3$ , amongst the products of these reactions is due to the oxidation of the  $\text{NO}$  produced in the synthesis, or of the undecomposed  $\text{NO}$  in the decomposition, by the oxygen present. Further, it became evident from these numerous investigations that the extent to which  $\text{NO}$  may be synthesised from its elements or decomposed into its elements depended mainly on the temperature at which the reaction was made to take place, and that the action of the electric spark or arc, the combustion of hydrogen, etc., in bringing about the synthesis or decomposition was due to the high temperature produced by these means.

In the synthesis of nitric oxide from nitrogen and oxygen we are dealing with a typical reversible reaction,



At any given temperature the reaction leads to an equilibrium. According to the law of mass-action, the following relation must exist between the concentrations of  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{NO}$  at equilibrium:—

$$K = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]},$$

where  $K$  is the equilibrium-constant, and the square brackets denote the concentrations of the enclosed substances. The value of  $K$  depends on the temperature, being constant for a given tem-

perature and independent of the composition of the original  $N_2-O_2$  mixture. The same value of  $K$  should, of course, be obtained for a given temperature, whether we start with a mixture of  $N_2$  and  $O_2$ , with pure NO, or with a mixture of  $N_2$ ,  $O_2$ , and NO. The concentration of NO at equilibrium for a given temperature is, however, dependent on the composition of the  $N_2-O_2$  mixture with which we start, and it can be shown that the maximum concentration is obtained by starting with a mixture of  $N_2$  and  $O_2$  in equimolecular proportions. This is readily seen from the equilibrium equation. Since  $K$  is constant, the value of the numerator is a maximum when the product  $[N_2][O_2]$  is a maximum, and, for a given total pressure, this is the case when  $[N_2] = [O_2]$ .

The effect of temperature on the equilibrium can be inferred from the heat of the reaction—



At ordinary temperature the formation of 2 gram-molecules of NO is accompanied by the absorption of 43,200 calories.<sup>8</sup> The reaction from left to right is, therefore, endothermic, and, according to van't Hoff's principle of mobile equilibrium, the equilibrium will be displaced by rise of temperature in favour of the formation of NO, the system formed with absorption of heat. With increasing temperature, therefore, the value of the equilibrium-constant  $K$  increases, and the concentration of NO present at equilibrium starting with a given  $N_2-O_2$  mixture, is the greater the higher the temperature.

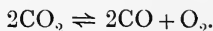
The relation between the equilibrium-constant  $K$  and the temperature is given by the equation—

$$\frac{d \log_e K}{dT} = \frac{-Q}{RT^2}.$$

Here  $Q$  is the heat of the reaction (in this case the heat of formation of 2 gram-mols. NO from 1 gram-mol.  $N_2$  and 1 gram-mol.  $O_2$ , namely  $-43,200$  cal.),  $T$  is the absolute temperature, and  $R$  the gas-constant, the numerical value of which is 1.985 when the gram-calorie is the unit of energy. On integrating between the absolute temperatures  $T$  and  $T_1$ , for which the respective equilibrium-constants are  $K$  and  $K_1$ , we obtain, on the assumption that  $Q$  is independent of the temperature, and on changing from natural to common logarithms,

$$\log_{10} \frac{K}{K_1} = \frac{Q}{2.3R} \left( \frac{T_1 - T}{TT_1} \right).$$

The first attempt to determine accurately this equilibrium was made by Muthmann and Hofer.<sup>9</sup> As the source of high temperature they used a high-tension alternating current arc. This was allowed to burn between platinum electrodes in a globe containing air long enough to ensure that equilibrium had been reached throughout the mass. The gases were then withdrawn and analysed. The temperature was determined by investigating under exactly similar conditions the dissociation of carbon dioxide into carbon monoxide and oxygen according to the equation—



From the observed degree of dissociation the temperature was obtained from the table given by Le Chatelier,<sup>10</sup> who determined the degree of dissociation of carbon dioxide over a considerable range of temperature. Muthmann and Hofer, however, regard the temperature so determined as a minimum only, and admit that it may be considerably below the real temperature. The equilibrium was also approached from the other side by exposing NO to the action of the arc for at least half an hour, and then withdrawing and analysing the gas mixture. The equilibrium-constant determined by this method agreed fairly well with that obtained by the synthetic method. Thus at 1800° the equilibrium-constants obtained were: from air,  $K = 8.97 \times 10^{-3}$ ; from nitric oxide,  $K = 7.90 \times 10^{-3}$ . The following table gives the mean value of the equilibrium-constant for different temperatures:—

Temp. C.	1825	1800	1590
$K$	0.0111	0.00841	0.000701

The concentration of nitric oxide at equilibrium and the equilibrium-constant increase with increasing temperature, which agrees with the result predicted by theoretical considerations. Muthmann and Hofer regarded the equilibrium in the arc as purely thermal.

Nernst gives reasons for believing that the temperature of the arc used by Muthmann and Hofer was much higher than the 1800° C. which they assume, and on account of the uncertainty of the temperature determinations a new and more accurate

investigation of the NO equilibrium was undertaken by Nernst<sup>11</sup> and his co-workers Finckh<sup>12</sup> and Jellinek.<sup>13</sup> A summary of the results obtained is given by Nernst.<sup>14</sup>

In the determination of such equilibria between gases at high temperatures, the gases leaving the reaction-chamber must be cooled to ordinary temperature before they can be analysed. If the cooling takes place slowly the equilibrium corresponding to the high temperature under investigation will be disturbed, and a new equilibrium reached for each temperature which the cooling gases assume, until a temperature is reached at which the velocity of the reaction is negligible. Below this temperature the composition of the gas mixture will undergo no further change, although the composition does not correspond to equilibrium at this temperature. If, however, the gases issuing from the reaction-chamber, in which equilibrium corresponding to the high temperature has been reached, are cooled rapidly enough to a temperature at which the reaction-velocity is negligible, it may be possible, by properly adjusting the rate of flow of the gases through the apparatus, to preserve at ordinary temperature the composition of the gases corresponding to equilibrium at the high temperature.

In the method employed by Nernst, dry atmospheric air was passed through a pipette-shaped platinum or iridium vessel contained in an electrically heated furnace which was maintained at a definite temperature. The gases left the reaction-chamber by means of a capillary outflow, in which the velocity

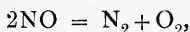


of flow of the gases was, therefore, increased compared with that in the reaction-chamber, thus hastening the passage of the gases through the danger-zone, in which a disturbance of the equilibrium might have occurred. The cooled gas leaving the capillary was then analysed, and the proportions of NO, N<sub>2</sub> and O<sub>2</sub> at equilibrium thus obtained. The equilibrium-constant for the particular temperature used could then be calculated. A full discussion of the problem of the preservation of the high temperature equilibrium and of the various criteria of equilibrium is given by Nernst<sup>11</sup> and by Haber.<sup>15</sup>

The equilibrium-constant  $K = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$  can also be determined from measurements of the velocity of decomposition of NO into N<sub>2</sub> and O<sub>2</sub>, and of the velocity of formation of NO from N<sub>2</sub> and O<sub>2</sub>. If in the decomposition of NO  $x$  is the concentration of NO present at time  $t$ , then the law of mass-action gives for the rate of decomposition of NO

$$-\frac{dx}{dt} = k_1[\text{NO}]^2 - k_2[\text{N}_2][\text{O}_2],$$

where  $k_1$  is the velocity-constant of the reaction



and  $k_2$  the velocity-constant of the reverse reaction.

At equilibrium  $-\frac{dx}{dt} = 0$ , and, therefore,

$$K = \frac{k_2}{k_1} = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}.$$

By determining the velocity-constants  $k_1$  and  $k_2$  for a given temperature, the equilibrium-constant  $K$  for

that temperature may be calculated. Such velocity determinations have been carried out by Nernst and Jellinek, and the possible concentration of NO from air at various temperatures calculated from them.

Finally, the equilibrium conditions for still higher temperatures have been calculated by Nernst<sup>16</sup> from experiments by Finckh, who measured the amount of NO produced by exploding mixtures of electrolytic gas ( $2\text{H}_2 + \text{O}_2$ ) and air. The following table gives the results obtained by these various methods:—

<i>T</i> abs.	<i>x</i> (obs.).	<i>x</i> (calc.).	Observer.
1811	0.37	0.35	Nernst
1877	0.42	0.43	Jellinek
2023	0.52-0.80	0.64	„
2033	0.64	0.67	Nernst
2195	0.97	0.98	„
2580	2.05	2.02	Nernst-Finckh
2675	2.23	2.35	„

The second column gives the observed equilibrium concentration of NO from air at the abs. temperature *T*. In the third column are given the calculated equilibrium yields of NO. These have been obtained from the equation—

$$\log_{10} \frac{K}{K_1} = \frac{Q}{2.3R} \left( \frac{T_1 - T}{TT_1} \right)$$

by taking the concentration of NO from air at 2200° abs. as 0.99 per cent. If *x* is the percentage of NO at equilibrium, starting with air (79.2 per cent. nitrogen and 20.8 per cent. oxygen), then

$$K = \frac{x^2}{\left(79.2 - \frac{x}{2}\right) \left(20.8 - \frac{x}{2}\right)}.$$

From this equation  $K$  can be calculated if  $x$  is known, and  $x$  if  $K$  is known. The close agreement between the observed and calculated values of  $x$  is a strong argument in favour of the process, as carried out by Nernst, being a purely thermal one.

From the velocity measurements of Jellinek the following table has been constructed:—

$T$ abs.	$k_1$ .	$k_2$ .	$t$ .
1000	$4.0 \times 10$	$1.74 \times 10^{-7}$	81.62 years
1500	$3.78 \times 10^4$	$2.33 \times 10^{-1}$	1.26 days
1900	$9.06 \times 10^6$	$1.20 \times 10^3$	2.08 mins.
2100	$1.40 \times 10^8$	$5.55 \times 10^4$	5.06 secs.
2500	$3.37 \times 10^{10}$	$6.98 \times 10^7$	$1.06 \times 10^{-2}$ sec.
2900	$8.07 \times 10^{12}$	$5.48 \times 10^{10}$	$3.45 \times 10^{-5}$ „

$k_1$  and  $k_2$  are the velocity-constants for the decomposition and formation of NO respectively at the absolute temperature  $T$ .  $t$  is the time required at  $T^\circ$  abs. for the formation of half the possible concentration of NO from air. On the other hand, the times required for the decomposition of half a given quantity of pure NO at atmospheric pressure are  $7.35 \times 10^3$  mins. at  $900^\circ$  abs.,  $5.80 \times 10^2$  mins. at  $1100^\circ$  abs., and  $4.43 \times 10$  mins. at  $1300^\circ$  abs. From these figures it is evident that the equilibrium between  $N_2$ ,  $O_2$ , and NO at very high temperatures is reached in an exceedingly short time, whilst at temperatures below about  $1000^\circ$  C. the rate of decomposition of NO is so slow as to be negligible in practice.

The theoretical considerations discussed above, which, as we have seen, are confirmed by the

experimental work of Nernst and his co-workers, indicated the conditions which must be observed in the technical production of nitric acid by the oxidation of atmospheric nitrogen. To obtain a high concentration of NO the air must be heated to as high a temperature as possible, and then cooled as rapidly as possible to a temperature at which the decomposition of NO takes place so slowly as to be practically negligible.

**The Formation of Nitric Oxide under the Influence of the Electric Discharge.**—For the attainment of the very high temperatures indicated by Nernst's work as necessary for producing high concentrations of NO, the most convenient means is the use of the electric arc, and this is the only method of bringing about the combination of nitrogen and oxygen which has met with technical success. The thermal explanation of the production of NO in the arc was for long universally accepted. The arc was regarded purely as a region of very high temperature, in which the thermal equilibrium was established practically instantaneously. The preservation of the high concentration of NO depended on the rapid removal of the equilibrium gases from the heated area and quick and efficient cooling. The more rapid the cooling the less was the decomposition of the NO formed at the high temperature. Occasional observations, such as those of v. Lepel,<sup>17</sup> indicating that electrical influences played a part in the production of NO in the electrical discharge, were ignored. The purely thermal explanation, first put forward by Muthmann and Hofer and supported

by the work of Nernst, received strong confirmation as the result of numerous subsequent investigations.

When a high-tension arc burns in air between horizontal electrodes a true flame is formed, the air-flame. This was observed by M'Dougall and Howles,<sup>18</sup> Muthmann and Hofer, and others, and its structure more closely investigated by Brode.<sup>19</sup> The flame consists of three zones: (1) a brightly luminous bluish band of light joining the electrodes, surmounted by (2), a broader bluish-green zone, and (3) a feebly luminous brownish zone above this. In zone (1) the current is carried, and this zone has the highest temperature, as it is the only part which derives its heat directly from the current. An idea of the temperature of this zone is got from the fact that concentrations of NO as high as 8 per cent. were obtained from air under special conditions with such a flame, and this corresponds, according to extrapolation from Nernst's figures, to a temperature of about 3700° C. According to Brode the high concentrations of NO correspond to thermal equilibrium in zone (1). In zone (3) NO at high concentration from the hotter parts of the flame undergoes partial decomposition. This is proved by the fact that higher concentrations of NO are got by cooling this zone, *e.g.*, by withdrawing the gases by a water-cooled capillary, and thus preventing decomposition as far as possible. Brode further showed that in zone (2) decomposition of ozone probably takes place. This view is supported by the following considerations. In nitrogen or hydrogen alone the discharge has the

form of a single blue band, corresponding to zone (1) of the air-flame. In pure oxygen there are two zones, apparently identical with (1) and (2) of the air-flame, and Brode succeeded in detecting ozone in the oxygen-flame. This proves that ozone is formed in the high-tension arc, and explains the flame formation in pure oxygen and the reaction in zone (2) of the air-flame.

**Evidence that the Reaction is purely Thermal.**—The most convincing evidence in favour of the purely thermal equilibrium in the high-tension arc discharge was furnished, however, by the work of Le Blanc and Nüranen<sup>20</sup> and of Grau and Russ.<sup>21</sup> Le Blanc and Nüranen, using a high-tension alternating current arc between horizontal electrodes of Nernst filaments, found that the expression—

$$\frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = K \text{ or } \frac{[\text{NO}]}{[\text{N}_2]^{\frac{1}{2}}[\text{O}_2]^{\frac{1}{2}}} = K_1$$

remained practically constant in spite of great differences in the composition of the initial  $\text{N}_2\text{-O}_2$  mixture (3.2 per cent. to 87.1 per cent.  $\text{O}_2$ ). They, therefore, conclude that the combination of nitrogen and oxygen to nitric oxide in the arc obeys the law of mass-action—a strong argument in favour of a purely thermal equilibrium. Grau and Russ, by using a vertical arc burning in water-cooled glass or silica tubes, were able to avoid the distortion of the arc to a flame which occurs when the arc is burned between horizontal electrodes, and to obtain steadily burning arcs up to 7 cms. long. Using such high-tension arcs, they investigated the

applicability of the law of mass-action to the formation of NO. The gases were withdrawn from the arc by a water-cooled platinum capillary, thus ensuring rapid cooling and preservation of the NO. At first they found that the value of the constant  $K$  increased with increasing oxygen content of the initial gas mixture, and concluded that with increasing oxygen content the temperature of the arc increased. In support of this assumption, they found that with an arc of given length and given current strength, the voltage, and, therefore, the watt-consumption, increased with increasing oxygen content of the initial mixture. In their subsequent work they, therefore, took equality of watt-consumption as a criterion of approximate equality of temperature in their arcs. By sucking off the gases from the arc with a cooled capillary, they found that with a high velocity of flow of the gases past the arc the concentration of the NO was small, as evidently an excess of air was used. With diminishing velocity of flow the concentration of NO increased. By extrapolation the concentration of NO for zero velocity was obtained, and this represents the equilibrium concentration of NO in the arc. This was found to be 5.5 per cent. NO from air and 6.6 per cent. NO from a mixture of equal volumes of  $N_2$  and  $O_2$ , independent of the length of the arc. The values of the equilibrium-constant  $K$  calculated from these figures agree to within about 4 per cent. Grau and Russ, therefore, conclude that the mass-action law holds. From the concentration of NO they calculated that the temperature of their

arc was ca.  $3500^{\circ}$  abs. They further showed that the equilibrium in the high-tension arc is not influenced by change of pressure (761-847 mm.) in agreement with the requirements of the law of mass-action for a reaction in which the number of molecules does not change. The effect of slow cooling of the gases is well seen in an experiment in which a concentration of 4.5 per cent. NO was obtained by sucking the gases from the middle of the arc, whereas just outside the arc, a few millimetres from the flame, the concentration was only 2.65 per cent. NO, indicating a decomposition of 40 per cent. of the original NO.

Another method of deciding whether the effect of the arc was purely thermal, or if electrical influences played a part in the formation of NO, was adopted by Foerster,<sup>22</sup> and by Lee and Beyer.<sup>23</sup> They argued that if electrical influences came into play, the yield of NO per unit of energy supplied to the arc should be different for a direct and an alternating current discharge. They found the yields to be practically identical, however, and concluded that the reaction in the arc was purely thermal.

Berthelot's statement,<sup>24</sup> that no nitrous gases are produced by the action of the silent electrical discharge on air, was also used in support of the thermal explanation. This statement was, however, contradicted by later work of Berthelot himself,<sup>25</sup> and especially by the work of Warburg and Leithäuser,<sup>26</sup> who showed definitely that NO was produced by the action of the silent discharge on air. In this case there is no doubt that the formation of NO is due



to electrical influences, since the experiments were carried out at ordinary temperature, at which the concentration of NO demanded by the thermal equilibrium is practically zero; and Warburg<sup>27</sup> expressed the opinion that the formation of NO in the arc was not a purely thermal process, but that electrical influences, *e.g.* electronic collisions, also played a part.

**The "Electrical" Production of Nitric Oxide.**—The most important contribution to the discussion of the relative importance of electrical and thermal effects in the production of NO in the high-tension arc is the brilliant experimental work of Haber and his co-workers. Haber and Koenig<sup>28</sup> seek to prove that the primary action in the high-tension arc, as in the silent discharge, is an electrical one—that the kinetic energy of the gaseous ions, and especially of the electrons produced in the arc, moving under the influence of the potential gradient between the electrodes, is utilised directly in the formation of NO when these ions and electrons collide with neutral molecules or with one another. The higher the potential gradient in the arc, the greater will be the kinetic energy of the moving ions and electrons, and the more effective the electrical production of NO. A condition which Haber and Koenig term an electrical equilibrium between nitrogen, oxygen, and nitric oxide will ultimately be reached, in which equal numbers of molecules of NO are formed and decomposed in a given time by electronic impacts. The electrical equilibrium differs from the purely thermal equilibrium. The position of the latter is

determined only by the temperature and the law of mass-action, whilst in an electrical equilibrium there is in addition a definite expenditure of electrical energy per unit of time, the amount of which determines the magnitude of the deviation from the purely thermal equilibrium for the same temperature. Since an electrical equilibrium is accompanied by an expenditure of free energy compared with the thermal equilibrium for the same temperature, we may say in general that the electrical equilibrium for a given reaction will correspond to the thermal equilibrium at a higher temperature. Thus the concentration of  $O_3$  in thermal equilibrium with  $O_2$ , of CO and  $O_2$  in thermal equilibrium with  $CO_2$ , of  $N_2$  and  $H_2$  in thermal equilibrium with  $NH_3$ , are infinitesimal at ordinary temperature. Under the influence of the silent discharge, however, concentrations of  $O_3$ , of CO and  $O_2$ , and of  $N_2$  and  $H_2$  corresponding to thermal equilibrium at much higher temperatures are obtained at ordinary temperature. Similar results were obtained by Warburg and Leithäuser for NO. They obtained measurable concentrations of NO by the action of the silent discharge on air at ordinary temperature, although the concentration of NO in thermal equilibrium with  $N_2$  and  $O_2$  at ordinary temperature is practically zero. That the concentration of NO corresponding to electrical equilibrium at ordinary temperature is preserved after the electrical influence is removed, is due merely to the extremely small velocity of decomposition of NO at ordinary temperature. If, on the other hand, the temperature is so high that the thermal equilibrium

is reached practically instantaneously, then the concentration of NO will correspond to the purely thermal equilibrium; for any excess of NO produced by the electrical equilibrium will immediately decompose owing to the rapidity with which the thermal equilibrium is reached. It therefore follows that the thermal phenomena can be subordinated to the electrical only in a temperature interval in which the decomposition velocity of NO is comparatively slow. Haber and Koenig realised these conditions by burning a high-tension, alternating current vertical arc under diminished pressure in a narrow water-cooled glass or quartz tube between electrodes of iron, platinum, or Nernst filaments. Under these circumstances the arc filled the narrow tube practically completely. Different mixtures of oxygen and nitrogen were passed *slowly* through the arc, the gas being made to enter and leave the tube some distance from the electrodes, so as to avoid the effects of the complex electrical conditions in the immediate neighbourhood of the electrodes. Under these conditions, concentrations of NO up to 9·8 per cent. were obtained from air, and up to 12·5 per cent. from a mixture of 4 vols. oxygen and 1 vol. nitrogen ("inverted air"). The pressures employed ranged from 25 to 140 mm., and it was found that the highest concentration of NO was got at a pressure of ca. 100 mm. With a mixture of equal volumes of nitrogen and oxygen a maximum concentration of 14·5 per cent. NO was obtained, and the same concentration was reached by passing pure NO through the arc under the same conditions. The main

arguments used by Haber and Koenig in support of the electrical theory of NO formation may be summed up as follows:—(1) A concentration of 9.8 per cent. NO corresponds, according to the thermodynamic calculation, to a temperature of ca.  $4100^{\circ}\text{C}.$ , and 12.5 per cent. to ca.  $4600^{\circ}\text{C}.$  Haber and Koenig give reasons for believing that the temperature of their arc was certainly below  $3000^{\circ}\text{C}.$ , and at most probably only a few hundred degrees above the melting point of platinum ( $1800^{\circ}\text{C}.$ ), a temperature at which the thermal equilibrium is comparatively immobile, so that NO formed by electronic collisions escapes thermal decomposition. (2) These high concentrations of NO were obtained when the gases were passed *slowly* through the arc, and no special precautions were taken to rapidly freeze the equilibrium. (3) According to the thermal explanation the results with air and “inverted air” should have been the same, whereas they differ very considerably. (4) That an electrical equilibrium was reached is proved by the identity of the results obtained, starting with pure NO and with a mixture of equal volumes of nitrogen and oxygen. Haber and Koenig, therefore, conclude that for the production of NO by the electrical discharge, the use of cold arcs will give the best results, and not, as hitherto held, the attainment of very high temperatures and rapid freezing of the equilibrium. The technical use of such arcs, however, offers very considerable difficulties, and up to the present they have not been introduced on a technical scale.

Haber and Koenig also critically examined

previous work on the production of NO in the high-tension arc in the light of their own results. With high-tension arcs burning between electrodes which are not too close together, the results obtained agree well apparently with the thermal explanation, since concentrations of NO are obtained which indicate a probable temperature of ca.  $3000^{\circ}\text{C}$ . for the arc. This temperature is calculated from Nernst's values for much lower temperatures, but the extrapolation is probably justified. Also the decomposition velocity of NO for such temperatures, extrapolated from the data of Nernst-Jellinek, do not exclude the attainment of the NO-concentrations reached in such arcs. According to Haber and Koenig, the apparent agreement with the thermal theory in these cases is due to secondary thermal decomposition, on account of the high temperature, of the NO produced electrically in the arc.

The matter is much more doubtful in the case of short high-tension arcs. With such alternating current arcs Muthmann and Hofer obtained NO-concentrations up to 6.7 per cent., Brode up to 7.2 per cent., and M'Dougall and Howles up to 7.4 per cent. Concentrations of ca. 7 per cent. correspond to a calculated temperature of ca.  $3500^{\circ}\text{C}$ . for the arc, a temperature which might quite well be reached as a result of the discharge. On the other hand, the thermal equilibrium at such temperatures is so mobile that it would be practically impossible to preserve these NO-concentrations even by rapid cooling. Haber and Koenig believe that in such arcs the high temperatures, calculated thermo-

dynamically, were not reached. They also show that in such high-tension, alternating current arcs the temperature must vary with enormous rapidity at every part of the arc, so that it is practically meaningless to speak of a mean temperature in such a case and apply it to the calculation of the thermodynamic equilibrium.

The results of Haber and Koenig for high-tension, alternating current arcs have been confirmed by Morden,<sup>29</sup> Holweh,<sup>30</sup> and Holweh and Koenig<sup>31</sup> for very short, direct current arcs with cooled anodes. The anode consisted of a water-cooled silver capillary, through which the gases were withdrawn. In some cases the cathode was specially heated, but this made no essential difference to the results. Concentrations of NO up to 9.5 per cent. were reached when the velocity of flow of the gases was made as small as possible. The most favourable pressure was 300-500 mm. The potential-gradient in the arc was carefully investigated, and it was found that, with a given length of arc, the stronger the field the greater was the maximum concentration of NO attainable, so long as the temperature of the arc was not too high. If the temperature was allowed to rise too much, thermal influences got the upper hand of electrical, and the maximum NO-concentration diminished. It was shown that the maximum temperature of the arc was probably about 3000° abs., which corresponds to a concentration of only ca. 4 per cent. NO for thermal equilibrium, whilst 9.5 per cent. NO would require a temperature of over 4000° abs., which was certainly not reached. Similar results were obtained

by Haber, Koenig, and Platou<sup>32</sup> using a 7.5 cm. direct current arc burning in a narrow, vertical water-cooled tube.

From a study of the admirable work of Haber and his collaborators, it is difficult to avoid the conclusion that the production of NO in the high-tension arc is primarily electrical, and that the comparatively low concentrations of NO in technical arcs are due to subsequent thermal decomposition of the electrically produced NO, owing to the high temperature conditions prevailing in such arcs.

Briner and Durand<sup>33</sup> and Guye<sup>34</sup> express the opinion that the thermal explanation is sufficient to account for the formation of NO in the arc. Their view is that our knowledge of the NO-equilibrium at high temperatures is based only on a wide extrapolation from values determined for much lower temperatures, and is, therefore, subject to all the uncertainties of such an extrapolation. Further, at high temperatures subsidiary reactions, such as dissociation of  $N_2$  and  $O_2$  to ions or atoms, probably take place. By the union of these ions or atoms greater concentrations of NO may be reached than are predicted by the extrapolation. Haber and Koenig quite admit this possibility, and, indeed, discuss it in their earlier papers. They maintain, however, that their results cannot be explained by the purely thermal theory, which demands for the highest concentrations of NO the highest arc temperature and the most rapid cooling. It is scarcely possible that in the cooled arcs traversed by a slow stream of gas which they employed, the temperature was higher

and the cooling more rapid than in the un-cooled arcs provided with special devices for rapidly freezing the equilibrium, used by previous investigators, who in every case obtained much lower NO-concentrations.

**Activation of Nitrogen and Oxygen prior to Formation of Nitric Oxide.**—Fischer and Hene<sup>35</sup> seek to prove that in the high-tension arc the oxidation of the nitrogen to NO is preceded by an activation of the oxygen, but not of the nitrogen. They suggest a chemical explanation for the high concentrations of NO obtained by Haber and Koenig in the cooled arc, and for the apparent deviations from the law of mass-action found by Grau and Russ<sup>21</sup> in presence of high concentrations of oxygen. They suggest that in both cases the conditions are favourable to ozone formation, and that it is the oxidation of the nitrogen by ozone which gives the high NO-concentrations. They were at first inclined to the view that an activation of the nitrogen, *e.g.* by dissociation into atoms at the high temperature, preceded the formation of NO. This suggestion was first put forward by Escales,<sup>36</sup> and was rendered probable by the discovery of an active form of nitrogen by Strutt,<sup>37</sup> who obtained it by the action of a jar-discharge with spark-gap on nitrogen under very low pressure. Strutt inclines to the view that his active nitrogen consists of nitrogen atoms. He finds, however, that it gives no NO with oxygen. Fischer and Hene, therefore, conclude that no activation of nitrogen in the arc takes place, and they regard this conclusion as confirmed by their experi-



mental work. The results on which they base their view that the formation of NO in the arc is due to an activation of the oxygen and not of the nitrogen are as follows: (1) With spark-discharge.—If the pure gas given in Column I. of the accompanying table is subjected to the spark-discharge whilst issuing from a quartz capillary, and the sparked gas leaving the capillary is immediately allowed to mix with the unsparked gas given in Column II., the relative concentrations of NO given in Column III. are obtained, the concentration from sparked  $N_2$  and unsparked  $O_2$  being taken as unity.

Sparked gas.	Unsparked gas.	Parts NO.
$N_2$	$O_2$	1.0
„	Air	1.5
Air	$N_2$	2.0
„	Air	3.5
„	$O_2$	4.0
$O_2$	Air	5.0
„	$N_2$	6.5

The concentration of NO from sparked  $O_2$  and unsparked  $N_2$ , for example, is 6.5 times that from sparked  $N_2$  and unsparked  $O_2$ . (2) With high-tension arc.—Air was passed through a high-tension arc burning between horizontal iron electrodes, and the air leaving the arc was immediately mixed with a current of ordinary oxygen, air, or nitrogen. Different concentrations of NO were obtained according to the gas used for mixing with the arced air. The concentrations of NO given in the

following table are calculated on the volume of air sent through the arc:—

Arced gas.	Unarced gas.	Per cent. NO by vol.
Air	N <sub>2</sub>	5·9
„	Air	7·4
„	O <sub>2</sub>	7·8

More NO is obtained, therefore, when air from the arc streams into oxygen and is cooled than when it streams into air or nitrogen. The different concentrations of NO might be explained by diffusion of the mixing gas into the arc flame. In that case the watt-consumption of the arc should have changed (Grau and Russ), which it did not. The increasing NO-concentration with increasing oxygen-content of the mixing gas must, therefore, be due to activation of the oxygen. (3) With silent discharge. — Ehrlich and Russ<sup>38</sup> found that both NO and O<sub>3</sub> were formed by the prolonged action of the silent discharge on air at ordinary temperature. It is not known certainly, however, whether O<sub>3</sub> oxidises nitrogen at ordinary temperature, as the reaction velocity is so slow. If the oxidation of nitrogen is attributed to the primary formation of O<sub>3</sub>, then the concentration of NO produced by the action of the silent discharge on air must be greater the higher the temperature, owing to the greater velocity of the reaction between ozone and nitrogen. Fischer and Hene passed air through an ozoniser which could be heated to a definite temperature, and obtained

the following concentrations of NO at different temperatures:—

Temp. C.	20°	380°	430°	510°	700°.
Per cent. NO	0.00	0.02	0.02	0.04	0.06.

No NO was formed at 700° without the discharge, and no O<sub>3</sub> was observed except at 20°, yet the concentration of NO increases with increasing temperature. From the results of these experiments Fischer and Hene conclude that the formation of NO in the high-tension arc is preceded by an activation of the oxygen. The energy supplied to the arc causes dissociation of the oxygen molecules to atoms. Outside the arc these atoms react with O<sub>2</sub>-molecules to form ozone. Whether the oxygen atoms also act directly with nitrogen cannot at present be determined. They point out that the reaction  $2\text{O}_3 + \text{N}_2 = 2\text{NO} + 2\text{O}_2$  is exothermic, liberating 250,000 cal. They suggest that better yields of NO might be obtained technically by passing pure oxygen through the arc instead of air, and then mixing it rapidly with nitrogen.

Koenig<sup>39</sup> criticises Fischer and Hene's conclusions that only the oxygen and not the nitrogen is activated in the arc. He points out that it is remarkable that, if no activation of nitrogen takes place, any NO at all should be obtained when sparked nitrogen mixes with unsparked oxygen. He considers that in no case was pure nitrogen or oxygen sparked, but that with the arrangement used by Fischer and Hene, owing to the rapid expansion and contraction of the gas in the capillary

during the high-frequency discharge, the mixing gas was drawn into the capillary, so that a mixture of nitrogen and oxygen was always sparked. The same doubt is expressed with regard to the high-tension arc experiments, where rapid expansion and contraction must also cause mixing of the gases. He maintains that admixture of 5 per cent. of oxygen with the air, which could easily raise the NO-concentration from 7.4 to 7.8 per cent., would hardly be shown with certainty by the watt-meter. He further asks why the experiments with the arc were not carried out according to the same scheme as with the spark, and especially why the crucial experiment of passing oxygen only through the arc and subsequently mixing it with nitrogen was omitted. Koenig concludes that Fischer and Hene have failed to prove their case. He points out that the facts that Strutt's active nitrogen does not react with oxygen, and that ordinary nitrogen is not oxidised by ozone, favour the view that a simultaneous activation of both gases must take place in order that they may react. These conditions are fulfilled in the arrangement used by Haber and Koenig,<sup>28</sup> where both gases are ionised.

Fischer and Hene reply to Koenig in a more detailed account of their work.<sup>40</sup> They explain the formation of NO when sparked nitrogen passes into unsparked oxygen by the production of active oxygen, by the action of the glowing nitrogen on the oxygen. The same explanation accounts for the difference between the action of arced air on oxygen and on nitrogen. In the former case new active oxygen is

formed by the action of the heated gas issuing from the arc, whilst in the latter case this is impossible. In support of the non-activation of the nitrogen they also quote Brode's observations on the appearance of the high-tension arc in different gases (p. 16), and the work of Compté<sup>41</sup> and Tiede,<sup>42</sup> who independently arrived at the conclusion that the phenomena attributed by Strutt to active nitrogen are really due to admixture of traces of oxygen with his nitrogen. Strutt,<sup>43</sup> however, maintained that this was not the case, and that the phenomena were observed with nitrogen free from every trace of oxygen, and this was confirmed by Koenig and Elöd.<sup>44</sup> The question whether active nitrogen really exists, or whether the phenomena accompanying its supposed production are due to admixture of traces of oxygen with the nitrogen, has been definitely settled.<sup>155</sup> Although absolutely pure nitrogen gives only a small yield of active nitrogen under the influence of the discharge, it has been proved beyond doubt that traces of oxygen are not necessary, although they have a marked beneficial effect on the production of active nitrogen. Traces of almost any gaseous impurity in the nitrogen, however, have a similar effect, largely increasing the yield of active nitrogen, probably by favouring the conditions in the discharge which give rise to it. Strutt has further shown that active nitrogen can be obtained from nitrogen at atmospheric pressure, although the yield is greatest at low pressures.

Although the results of Fischer and Hene are of great interest, it is difficult, from a study of their

apparatus, to avoid the suspicion that mixing of the gases did take place to some extent, and Koenig and Elöd<sup>156</sup> have given further experimental evidence that it does actually take place.

Koenig and Elöd<sup>157</sup> found that when pure dry ozone-free oxygen was submitted to the discharge in the same apparatus as was used for activating nitrogen, it gave a weak bluish-green afterglow, not so persistent as that of nitrogen. If this glowing oxygen was mixed with glowing (active) nitrogen from another apparatus, oxides of nitrogen were produced. If the arc was extinguished in either apparatus, no further formation of oxides of nitrogen took place. They therefore concluded that an active modification of oxygen was formed, different from ozone and capable of existing for a short time only, and that the formation of nitric oxide in the arc was preceded by an activation of both the nitrogen and the oxygen.

An important contribution to the question of the mechanism of NO-formation by the electrical discharge was made by Lowry.<sup>45</sup> He described experiments in which a current of air was submitted to the action of the silent discharge in an ozoniser, or to the action of the spark-discharge, or to a combination of the two. A very delicate spectroscopic method, depending on the photographing of the NO<sub>2</sub>-spectrum in a column of gas 64 ft. long, was used to detect NO<sub>2</sub> in the air so treated. A concentration of NO<sub>2</sub> of  $\frac{1}{8000}$  part by volume could be detected with certainty. Under ordinary conditions no NO<sub>2</sub> was found when air was passed

through the ozoniser alone or through three spark-gaps alone. When the air was passed first through the ozoniser and then through the spark-gaps,  $\text{NO}_2$  was formed. This agreed with the observation of Cramp and Hoyle<sup>46</sup> that the yield of  $\text{NO}_2$  from the arc discharge can be increased by ozonising the air supply. An almost equal concentration of  $\text{NO}_2$  was obtained, however, by passing the air first through the spark-gaps and then through the ozoniser. This was surprising, as ready-made  $\text{NO}_2$  is bleached by passing through the ozoniser, being probably oxidised to  $\text{N}_2\text{O}_5$  or  $\text{HNO}_3$ . It was next found that a spectrum of only slightly less intensity was got by passing air currents through the ozoniser and spark-gaps in parallel, and then mixing the two air currents. From a critical examination of these facts Lowry concludes that they can be explained only by assuming that the spark-discharge produces an oxidisable form of nitrogen ("atomised" or "ionised" nitrogen), which is readily oxidised by ozone, but not by oxygen. The most efficient way to oxidise it is to produce it in an atmosphere already charged with ozone; rather less efficient is to pass the air in which it is produced directly into the ozoniser; less efficient still is where the oxidisable nitrogen is mixed with ozonised air in a chamber a few feet away from the discharge apparatus. The slight but clearly marked gradation in the amount of  $\text{NO}_2$  produced in these three cases is evidence of the instability of the oxidisable nitrogen, which appears to revert in a few seconds to a form which is oxidisable neither by oxygen nor by ozone. These experiments

seem to prove that an active variety of nitrogen can be produced by the electrical discharge in air at ordinary pressure. It differs from Strutt's active nitrogen, which gives no oxides of nitrogen with ozone. In view of his results, Lowry thinks it is not unreasonable to ask whether the production of oxides of nitrogen by the electrical discharge in all its forms is not due to the interaction of active nitrogen and active oxygen, either as ozone or atomic oxygen. His work strongly supports Haber and Koenig's view that both the oxygen and nitrogen are activated in the high-tension arc.

**The Yield of Nitric Acid in the Arc.**—By the yield of nitric acid is meant the quantity of acid produced per unit of electrical energy expended in its production, and is generally expressed in grams  $\text{HNO}_3$  per kilowatt-hour or in kilograms  $\text{HNO}_3$  per kilowatt-year. A high concentration of NO in the gases leaving the arc does not necessarily mean a high yield of  $\text{HNO}_3$ . Thus when the velocity of passage of the air through the arc is large, much of the gas does not enter the arc or become strongly heated. The portion of the air which has been highly heated by contact with the arc, and which contains much NO, is, however, rapidly cooled by mixing with the excess of cold air, and the decomposition of the NO is thus prevented to a large extent. With a less rapid flow of air through the arc at the same temperature, the concentration of NO in the issuing gas may be greater on account of the smaller dilution with excess of cold air, but, owing to less efficient cooling, a larger proportion of the NO formed at the highest



temperature of the arc will be lost by decomposition, and the yield of  $\text{HNO}_3$  may be less than with a high velocity of flow. Too great dilution with cold gas must, however, be avoided, since the more dilute the gas, the larger the proportion of oxides of nitrogen which escape absorption. Assuming that the reaction in the arc is a purely thermal process, several investigators have calculated the theoretical yield of  $\text{HNO}_3$ . Thus Haber,<sup>47</sup> assuming the temperature of the arc to be  $4200^\circ\text{C}$ ., calculates as follows. From the thermodynamic extrapolation the composition of the equilibrium mixture at this temperature, starting with air, is 10 per cent.  $\text{NO}$ , 16 per cent.  $\text{O}_2$ , 74 per cent.  $\text{N}_2$ . Ten mols. of  $\text{NO}$  will yield by a series of spontaneous reactions 630 grams of  $\text{HNO}_3$ . To get this amount of  $\text{HNO}_3$  we must, therefore, heat 100 mols. of  $\text{N}_2$  and  $\text{O}_2$  to  $4200^\circ\text{C}$ . Assuming the specific heat per mol. of the permanent gases at the temperature  $t^\circ\text{C}$ . to be represented by the formula  $6.8 + 0.0006t$ , we find the amount of heat required to raise the 100 mols. to  $4200^\circ\text{C}$ . to be—

$$100(6.8 + 0.0006 \times 4200)4200 = 3,914,400 \text{ cal.}$$

To this must be added—

$$10 \times 21600 = 216,000 \text{ cal.,}$$

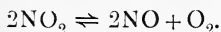
the heat of formation of 10 mols. of  $\text{NO}$  from  $\text{N}_2$  and  $\text{O}_2$ . The total heat expenditure is, therefore, 4,130,400 cal. = 4.71 kilowatt-hours for 630 grams  $\text{HNO}_3$ . The yield is, therefore, 134 grams  $\text{HNO}_3$  per kilowatt-hour, or 1174 kilos.  $\text{HNO}_3$  per kilowatt-year. A similar calculation for a tempera-

ture of  $3200^{\circ}\text{C}$ . gives 93.5 grams  $\text{HNO}_3$  per kilowatt-hour, or 819 kilos. per kilowatt-year. Lowering the temperature thus diminishes the possible yield. On the other hand, there will be a smaller loss of NO owing to decomposition during cooling at the lower temperature, and the loss of heat by radiation will be much less at  $3200^{\circ}$  than at  $4200^{\circ}\text{C}$ .

It is of interest to compare the yields obtained by different investigators. Rayleigh,<sup>48</sup> who burned the arc in a mixture containing 36 per cent.  $\text{N}_2$  and 64 per cent.  $\text{O}_2$ , obtained ca. 50 grams  $\text{HNO}_3$  per K.W.H. M'Dougall and Howles,<sup>18</sup> who were the first to thoroughly investigate the production of  $\text{HNO}_3$  from air, obtained 34 grams  $\text{HNO}_3$  per K.W.H. from air, and 67 grams from the mixture used by Rayleigh. The doubling of the yield they attribute to mass-action, but, according to Haber,<sup>49</sup> this explanation is insufficient. They also found that the yield increased with the watt-consumption (increased current-strength) only up to a certain point, beyond which it remained practically stationary, the excess of electrical energy being lost by radiation and conduction. This result was confirmed by Scheuer<sup>50</sup> and by Grau and Russ, who obtained, with their vertical arcs, 52 grams  $\text{HNO}_3$  per K.W.H. with a 3 cm. arc, and 62 grams with a 5 cm. arc, and concluded that longer arcs would give even higher yields. They also showed that a higher yield was obtained from a mixture of equal volumes of nitrogen and oxygen than from air, as required by the law of mass-action. The yields obtained with the alternating-current cooled arcs used by Haber

and Koenig were investigated by Haber, Koenig, and Platou. A yield of 57 grams per K.W.H. was reached, the concentration of NO being 3.4 per cent. Much higher yields were obtained with the cooled direct current arc. Thus Morden obtained up to 90 grams per K.W.H., Holwech, and Holwech and Koenig up to 80 grams per K.W.H. Although these yields do not differ greatly from those in technical arcs (60-75 grams per K.W.H.), they are obtained with much more favourable NO - concentrations. Thus Holwech obtained 60-70 grams per K.W.H. with ca. 4 per cent. NO, whilst the NO-concentration reached in technical work is only ca. 2 per cent. This Holwech attributes to the much steeper potential gradient used in his arc, and consequent increased ionisation.

**Oxidation of Nitric Oxide.**—Richardson<sup>51</sup> showed that NO<sub>2</sub> begins to dissociate into nitric oxide and oxygen above ca. 140° C. The degree of dissociation increases with increasing temperature, and at ca. 620° C., under ordinary pressure, the dissociation is complete according to the equation—



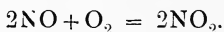
The following table shows the degree of dissociation at various temperatures and ordinary pressure—

<i>t</i> ° C.	184°	279°	494°	620°.
Per cent. NO <sub>2</sub> dissociated	5.0	13.0	56.5	100.0.

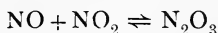
The oxidation of NO formed at the high temperature of the arc does not begin, therefore, until the tempera-

ture has fallen below  $620^{\circ}$ , and cannot be complete above ca.  $140^{\circ}$ .

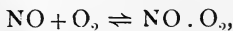
According to Raschig<sup>52</sup> the oxidation takes place in two stages. The first reaction corresponds to the formation of  $N_2O_3$  and takes place rapidly, whilst in the second stage the  $N_2O_3$  is more slowly oxidised to  $NO_2$ . Lunge and Berl,<sup>53</sup> on the other hand, found that the oxidation took place with measurable velocity as a trimolecular reaction according to the equation—



Nitrogen trioxide cannot be formed in any considerable concentration during the oxidation, since, under ordinary conditions, it is practically completely dissociated into NO and  $NO_2$ .<sup>54</sup> The work of Schmidt and Böcker<sup>55</sup> and of Le Blanc<sup>56</sup> indicates, however, that in a mixture of NO and  $NO_2$ —and such a mixture is formed during the oxidation of NO by air—the equilibrium



exists. The concentration of  $N_2O_3$  at equilibrium is, however, very small. Foerster and Blich<sup>57</sup> found that the velocity of oxidation of NO by oxygen has a small negative temperature coefficient between  $0^{\circ}$  and  $100^{\circ}$ . They explain this by assuming that a “primary” oxide is first formed, *e.g.*—

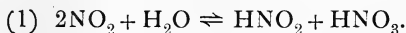


which then reacts with a second molecule of NO to give  $NO_2$ —

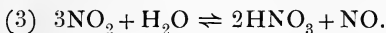


The first reaction is reversible, and tends to an equilibrium, which, with increasing temperature, favours the dissociation of the "primary" oxide. The smaller concentration of the latter at the higher temperature more than counteracts the greater velocity of the reaction between "primary" oxide and NO. Holwech<sup>58</sup> also found that the oxidation of NO to NO<sub>2</sub> was a comparatively slow reaction. The most accurate investigation of this important reaction we owe to Bodenstein.<sup>158</sup> He showed that the reaction was trimolecular, as formulated by Lunge and Berl, and was able to explain the discrepancy between the results of Raschig and Lunge and Berl. He determined the velocity constant for the reaction at various temperatures and confirmed the small negative temperature coefficient found by Foerster and Blich. Raschig's results are due to an error in his method, and his explanation of the reaction is no longer tenable.

**Absorption of Oxides of Nitrogen by Water.**—A thorough investigation of the action of NO<sub>2</sub> on water was made by Foerster and Koch.<sup>59</sup> (A discussion of previous work is also given in their paper.) The formation of HNO<sub>3</sub> by the action of NO<sub>2</sub> on water is represented by the following reversible reactions:—



The total reaction is—



According to the law of mass-action, therefore,

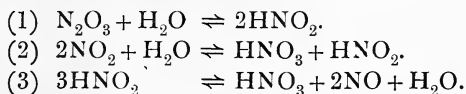
definite partial pressures of  $\text{NO}_2$  and of  $\text{NO}$  correspond to a given concentration of  $\text{HNO}_3$ . The  $\text{NO}$  and  $\text{NO}_2$  pressures are, however, influenced by the equilibrium  $\text{NO} + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_3$ , and by the solubility of  $\text{N}_2\text{O}_3$  in concentrated  $\text{HNO}_3$ , especially at low temperatures. Further, in presence of excess of oxygen equilibrium (2) and, therefore, also equilibrium (1) is continuously disturbed by the reaction  $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ , so that a given quantity of  $\text{NO}_2$  must ultimately be completely converted into  $\text{HNO}_3$ . Foerster and Koch show that when a mixture of nitrogen peroxide and oxygen, prepared from 1 vol.  $\text{NO}$  and 2 vols.  $\text{O}_2$ , is led into water, the formation of  $\text{HNO}_3$  takes place very rapidly until the concentration of  $\text{HNO}_3$  is ca. 40 per cent. The absorption of nitrogen peroxide then becomes gradually slower until 50 per cent.  $\text{HNO}_3$  is reached, beyond which concentration the rate of absorption rapidly diminishes. At ordinary temperature it is not possible to obtain a stronger acid than 68-69 per cent. by the action of nitrogen peroxide and oxygen on water. This limiting concentration of  $\text{HNO}_3$  is explained by the diminution of the active mass of free water with increasing concentration of  $\text{HNO}_3$ , owing to hydrate formation with  $\text{HNO}_3$ , which diminishes the velocity of reaction (3), and to the increasing concentration of  $\text{HNO}_3$  vapour in the gaseous phase with increasing concentration of the aqueous acid. The stronger the acid, the more  $\text{HNO}_3$  does the gas current remove in the vapour it carries along with it. The concentration of  $\text{HNO}_3$  reached is due to an equilibrium between these various factors. The lower the con-

centration of  $\text{NO}_2$  in the gas mixture, the lower will be the limiting concentration of  $\text{HNO}_3$  attainable, since the velocity of the reaction between  $\text{NO}_2$  and water diminishes with diminishing  $\text{NO}_2$  concentration, whilst the presence of a large excess of foreign gases accelerates the evaporation of  $\text{HNO}_3$  from the solution. The following limiting concentrations of  $\text{HNO}_3$  were obtained at ordinary temperature from air containing various amounts of  $\text{NO}_2$  :—

Per cent. $\text{NO}_2$ in air	1	2	5
conc. $\text{HNO}_3$	ca. 46	ca. 52	>55 per cent.

Since the concentration of  $\text{NO}_2$  in the gases produced technically by the combustion of nitrogen in the arc contain 1-2 per cent.  $\text{NO}_2$ , it should be possible to obtain 46-52 per cent.  $\text{HNO}_3$  by absorption with water.

Briner and Durand<sup>60</sup> studied the effect of temperature and pressure on the equilibrium between nitric and nitrous acids and oxides of nitrogen. They conclude that this equilibrium comprises three reversible reactions—



The action of  $\text{NO}$  on  $\text{HNO}_3$  tends to produce nitrous anhydride; the greater the pressure of  $\text{NO}$ , and the greater the concentration of  $\text{HNO}_3$ , the more readily does this take place. The effect of increase of temperature is to lower the ratio  $\text{HNO}_2:\text{HNO}_3$ , since reaction (3) is endothermic. High pressure and low temperature, therefore, favour the formation of

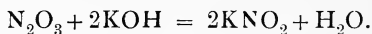
$\text{HNO}_2$ , and the reverse conditions the formation of  $\text{HNO}_3$ . The equilibrium corresponding to equation (3) has also been investigated by Ssaposhnikoff,<sup>61</sup> and more recently by Lewis and Edgar.<sup>62</sup>

The velocity of decomposition of nitrous acid according to equation (3) above, has been studied by Knox and Reid.<sup>159</sup> They found that the velocity was increased by agitation, rise of temperature, and presence of excess of air, which removes the nitric oxide. These results are of importance in the manufacture of nitric acid by the absorption of nitrous gases in water, since nitrous acid is always an intermediate product.

**Absorption of Oxides of Nitrogen by Alkalies.**—When nitrogen peroxide is absorbed by alkalies, a mixture of nitrate and nitrite in practically equimolecular proportions is obtained—



A mixture of NO and  $\text{NO}_2$  in equimolecular proportions behaves as  $\text{N}_2\text{O}_3$ , and gives on absorption by alkalies practically pure nitrite, together with a little nitrate and NO.<sup>63</sup>



When a mixture of nitric oxide and air or oxygen is absorbed by alkali, nitrite predominates, and the sooner the absorption takes place after admixture the greater is the proportion of nitrite found. Thus when air containing nitric oxide from the arc flame is passed through potassium hydroxide solution, nitrite is always in excess of nitrate, and the excess is greater when the gases are sucked directly out



of the flame and absorbed at once. Le Blanc<sup>56</sup> explains this behaviour by assuming that during the absorption of a mixture of nitric oxide and air by alkali, in which the NO is undergoing oxidation to NO<sub>2</sub>, the following reactions take place:—

- (1)  $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$ .
- (2)  $\text{NO} + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_3$ .
- (3)  $2\text{NO}_2 + 2\text{KOH} = \text{KNO}_3 + \text{KNO}_2 + \text{H}_2\text{O}$ .
- (4)  $\text{N}_2\text{O}_3 + 2\text{KOH} = 2\text{KNO}_2 + \text{H}_2\text{O}$ .

Reactions (2) and (4) take place rapidly, and although the concentration of N<sub>2</sub>O<sub>3</sub> in the gas is always small (p. 40), the equilibrium is continually disturbed by the absorption of the N<sub>2</sub>O<sub>3</sub>. Fresh quantities are formed from NO and NO<sub>2</sub>, and this goes on until either the NO or the NO<sub>2</sub> is exhausted. Reaction (3) is comparatively slow.<sup>64</sup> Foerster and Blich<sup>57</sup> confirmed Le Blanc's assumption that in a gas in which only part of the NO is oxidised to NO<sub>2</sub>, the equilibrium  $\text{NO} + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_3$  exists, and that alkali absorbs principally N<sub>2</sub>O<sub>3</sub> from such a mixture, so that it behaves to alkali as if it consisted of N<sub>2</sub>O<sub>3</sub>. They showed that liquid N<sub>2</sub>O<sub>3</sub> is absorbed much more rapidly by alkali than N<sub>2</sub>O<sub>4</sub>. A mixture of NO and NO<sub>2</sub> is, therefore, much more rapidly and completely absorbed by alkali than pure NO<sub>2</sub>.

These considerations explain the technical production of almost pure nitrite when the hot gases from the arc are absorbed by alkali. Such hot gases contain a mixture of NO and NO<sub>2</sub>, since above 140° the oxidation of NO cannot be complete (p. 39). In a mixture of NO and air, in which the concentration

of NO is very small, the velocity of oxidation of NO to  $\text{NO}_2$  will be very slow, in accordance with the law of mass-action. Such a mixture leaves the last of the acid absorption towers in the technical production of  $\text{HNO}_3$  from air. At the rate at which the gas current is passed through the absorption apparatus, there is insufficient time for the complete oxidation of the NO before the gas current reaches the alkali absorption towers, so that in them mainly nitrite is formed.

By the action of ozone on nitrogen peroxide Helbig<sup>65</sup> found that  $\text{N}_2\text{O}_5$  was rapidly formed, which can be absorbed by water giving concentrated  $\text{HNO}_3$ . Foerster and Koch<sup>59</sup> also found that ozone oxidises  $\text{NO}_2$ , even when very dilute, very rapidly to  $\text{N}_2\text{O}_5$ . By leading a mixture of dilute  $\text{NO}_2$  and ozone into water it is easy to get  $\text{HNO}_3$  of more than 80 per cent. strength. Owing to the great velocity of the reaction between  $\text{NO}_2$  and  $\text{O}_3$ , the addition of ozonised air might be utilised technically for the conversion of the very dilute nitrous gases leaving the absorption towers into  $\text{HNO}_3$ . At present, however, ozone evidently cannot be produced sufficiently cheaply to make its use remunerative.

### Technical Manufacture of Nitrates and Nitrites.

Of the innumerable processes and forms of apparatus which have been patented<sup>66</sup> for effecting the union of nitrogen and oxygen by means of the electrical discharge, only those which have met with technical success can be described here. Among the pioneers of the synthetic nitrate industry must

be mentioned P. A. Guye and his co-workers C. P. Guye and Naville,<sup>67</sup> who, since their first patents in 1895, have made constant improvements in their apparatus, and have contributed materially to the solution of the problem of synthesising nitric acid from air. The work of Moscicki and Kowalski<sup>68</sup> must also be noticed. Great ingenuity has been displayed in the design of their furnaces, some of which, from tests on a small scale, give promise of technical success.

The earlier inventors aimed at rapidly heating the air to as high a temperature as possible and quickly cooling it. To avoid heat losses as much as possible they used a large number of low-current, high-tension arcs instead of a single heavy-current arc. By suitable arrangements a large number of long, slender arcs were made to form, expand through a large volume of air and break, so that rapid heating and cooling was ensured. The first attempt to work such an apparatus on a technical scale was made by Bradley and Lovejoy<sup>69</sup> in 1902, at Niagara Falls, but failed owing to high initial cost, the small units which were employed, and the heavy repair charges caused by the complicated nature of the apparatus.

The processes at present in successful technical operation depend on the concentration of large amounts of energy in a single heavy-current discharge. The apparatus is marked by simplicity and compactness, which allows the use of much larger units than in the earlier apparatus. Of these processes the most important are the Birkeland-Eyde, the Schönherr, and the Pauling.

**The Birkeland-Eyde Process.** <sup>3, 70, 71</sup>—The principle on which the Birkeland-Eyde furnace depends is as follows. If a direct-current arc is burned between electrodes which are placed in the field of a powerful direct-current electromagnet, so that the direction of the magnetic field is perpendicular to that of the arc, then the arc moves in a direction at right angles to the magnetic lines of force. The ends of the arc retreat along the electrodes and the path of the arc assumes a semi-circular form. As the arc lengthens its resistance increases, and the voltage rises until a new arc strikes across between the electrodes. Owing to the smaller resistance of the short arc the voltage sinks, and the long arc is finally extinguished when the tension is no longer able to maintain it. The same process is repeated with the new arc, and so on. We thus get a series of arcs starting between the electrodes and moving rapidly outwards until they are extinguished, so that the discharge presents the appearance of a thin semi-circular sheet of flame. If the horizontal electrodes are supplied with alternating current instead of direct, the arc will be deflected upwards when the current passes in one direction, and downwards when in the other. The discharge then presents the appearance of a circular sheet of flame (Fig. 1). To steady the arc it is necessary to have an inductive resistance in series with it. The Birkeland-Eyde furnace consists of a sheet-steel chamber in the form of a low, wide cylinder resting on its side. This is lined internally with fire brick so as to leave a narrow disc-shaped space in the centre about 2 m.

in diameter and 5-10 cm. wide. The electrodes enter this space radially, one from each side, along a horizontal diameter, whilst the poles of the large electromagnet are set in the axis of the cylinder, embedded in the refractory lining, so that the direction of the magnetic field is perpendicular to the plane of the central space. The electrodes are

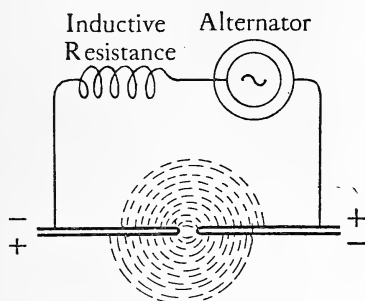


FIG. 1.

copper tubes, cooled by water circulation, and are placed about 1 cm. apart. They are supplied with alternating current at ca. 5000 volts and 50 periods per second, whilst the coils of the electromagnet are supplied with direct current. The flame sheet produced is about 1.8 m. in diameter. A current of air is driven through the furnace by a Root blower. It enters the flame-chamber from both sides through perforations in the refractory lining, passes radially along the flame and leaves by a peripheral channel in the furnace lining. Fig. 2 shows a section of the later type of furnace; the arrows indicate the direction of the air current.

Furnaces taking up to 3000-4000 kilowatts are in operation. The electrodes are changed for repair after about 300 hours' use. This can be rapidly effected. The furnace lining requires attention only once or twice a year, since, in spite of the very high temperature of the flame (ca.  $3200^{\circ}$ ), the walls are kept comparatively cool by the air current.

The gas current leaving the furnace has a temperature of  $800^{\circ}$ - $1000^{\circ}$ , and contains 1-1.5 per cent. NO.

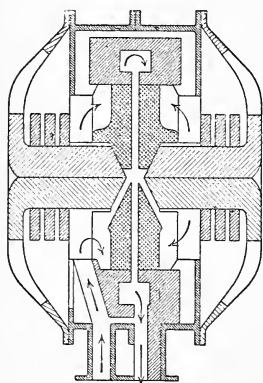


FIG. 2.

It is led first into a large iron main lined with fire-brick, which passes into an aluminium main. This leads to a large vat, where the single main divides into a large number of small aluminium tubes, thus exposing a large cooling surface. Water is heated or solutions evaporated in the vat by the heat of the gases. The gas leaving the vat is collected in

a single main leading to the boiler-house, where the hot current is passed through tubular boilers and raises large quantities of steam, which can be used for evaporation, etc. The gas leaving the boilers has a temperature of about  $200^{\circ}$  C. It is cooled to about  $50^{\circ}$  C. by being passed through a series of aluminium tubes over which cold water is flowing. It then enters the oxidation chambers, two large iron cylinders lined with acid-proof material. Here the rate of flow of the gases is checked and time given

for the completion of the oxidation of  $\text{NO}$  to  $\text{NO}_2$ . This is necessary, as with dilute gases the time required for complete oxidation is considerable. Thus a mixture of air with 2 per cent.  $\text{NO}$  requires about twelve seconds for the oxidation of 50 per cent., and one hundred seconds for the oxidation of 90 per cent. of the  $\text{NO}$ . By means of powerful fans the gas from the oxidation chambers is sent to the absorption towers, enormous granite towers filled with fragments of quartz and provided at the top with an arrangement for distributing the absorbing liquid. In these towers the  $\text{NO}_2$  is converted to  $\text{HNO}_3$  by the action of water and excess of air (p. 41). A series of three such towers is used at Notodden. The gas traverses the three towers in succession, entering at the bottom and leaving at the top. The absorbing liquid is sent in the opposite direction. When the  $\text{HNO}_3$  in the third tower has reached its maximum concentration it is transferred to the second and replaced by water. The liquid from the second tower goes to the first, the solution being raised from the bottom of one tower to the reservoir at the top of the next by compressed air. The acid leaving the first tower has a concentration of about 30 per cent., and in the succeeding towers it is more and more dilute. The acid from the first tower is stored in large granite reservoirs. The gases leaving the last acid tower still contain oxides of nitrogen—up to 15 per cent. of the original  $\text{NO}$ . These are absorbed by alkaline liquids in one or more alkali towers, the absorption by alkali being much more rapid and complete than with water. The

wooden alkali towers are filled with brick, and the product obtained depends on the conditions of absorption. If the NO is allowed sufficient time for more or less complete oxidation to  $\text{NO}_2$  in its passage from the last acid tower to the alkali tower, a mixture of approximately equal proportions of nitrate and nitrite results. Formerly milk of lime was used as absorbent, and the resulting nitrate-nitrite mixture was decomposed by  $\text{HNO}_3$ , giving pure  $\text{Ca}(\text{NO}_3)_2$  and oxides of nitrogen, which were returned to the acid towers. At present  $\text{Na}_2\text{CO}_3$  or  $\text{NaOH}$  solution is used as absorbent. Insufficient time is given for complete oxidation of the NO, so that a mixture of NO and  $\text{NO}_2$  enters the alkali towers. A solution of  $\text{NaNO}_2$  is thus obtained (p. 45), which is evaporated, crystallised, and the nearly pure nitrite crystals dried in a centrifugal machine. The gas leaving the alkali towers still contains small quantities of oxides of nitrogen (about 2 per cent. of the original NO), and these at present are lost. The arrangements for absorption are practically the same in all the factories, although differences in detail occur.

The  $\text{HNO}_3$  from the first tower is utilised in various ways. Much of it is converted into calcium nitrate by neutralisation with limestone. The resulting solution is evaporated by the waste heat from the furnace gases until the temperature reaches ca.  $140^\circ\text{C}$ . The solution is then allowed to solidify. The solid contains about 80 per cent. anhydrous  $\text{Ca}(\text{NO}_3)_2$ , or about 13 per cent.  $\text{N}_2$ , and is used as a manure (nitrate of lime, air saltpetre, Norwegian saltpetre). Owing to the hygroscopic nature of the



neutral nitrate, which is against its use as a manure, various attempts were made to overcome the difficulty. For a time the partly dehydrated neutral nitrate was mixed with a certain proportion of  $\text{Ca(OH)}_2$ . This gave a fertiliser which was but slightly hygroscopic. The use of the basic nitrate seems, however, to have been abandoned. If the solution of  $\text{Ca(NO}_3)_2$  is evaporated until the temperature reaches  $120^\circ\text{C}$ ., it gives on crystallisation pure  $\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , which is used in the preparation of  $\text{Ba(NO}_3)_2$ , large quantities of which are required for the manufacture of fireworks and of barium peroxide. Much of the nitric acid produced by the Birkeland-Eyde process was used in the preparation of  $(\text{NH}_4)\text{NO}_3$ , by the neutralisation of the  $\text{HNO}_3$  with ammonia-water, brought direct from Britain.

**The Pauling Process.**<sup>71, 72</sup>—In the furnace invented by H. and A. Pauling the hollow electrodes (a)

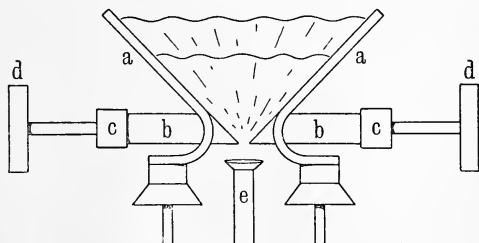


FIG. 3.

(Fig. 3) are water-cooled and set at an angle of  $90^\circ$ . At the lowest point they are about 4 cm. apart, so as not to interfere with the air blast from the nozzle *e*. Through vertical slits in the lowest part of the electrodes thin iron blades *b* are inserted.

These so-called "kindling blades" or "ignition knives," the ends of which are only 2-3 mm. apart, serve to start the arc, which is maintained by a high-tension alternating current. The very thin blades do not interfere with the air blast. At each half period a new arc is formed, which, in consequence mainly of the blast of heated air from *e*, runs along the divergent electrodes until it is extinguished. It is followed by others in rapid succession, so that the result is a continuous sheet of flame about 3 ft. high. The distance between the ignition knives is constantly adjusted by the mechanism *c d* as they burn away. They last about twenty hours and can be rapidly replaced. The main electrodes last about two hundred hours. In the later furnaces the electrodes are very close together, and no auxiliary starting circuit is needed. Two such arcs in series are contained in each furnace, which is made of refractory material. Fig. 4 shows two sections of such a furnace in directions at right angles to each other. Air enters by A, and the mixture of air and NO leaves by the common outlet B. Through the hollow dividing wall C between the two arcs, cold air which has already been through the furnace is sent into the upper part of the flame. It serves to rapidly cool the gases from the flames without diluting them, and as it enters at a lower pressure than the main current which passes the arcs, it helps to heighten and broaden the flame by its suction effect. The gases leaving the furnace by B have a temperature of about 1000°, and contain about 0.8 per cent. NO. They are used to preheat the entering air, and then

pass to two large cooling towers filled with fire-brick. When the bricks in one tower have become sufficiently hot, the current is switched to the second tower, whilst the first is cooled by drawing a current of fresh air through it. The gases then pass through an aluminium cooler to the oxidation chambers. Part of the gas from the oxidation chambers is

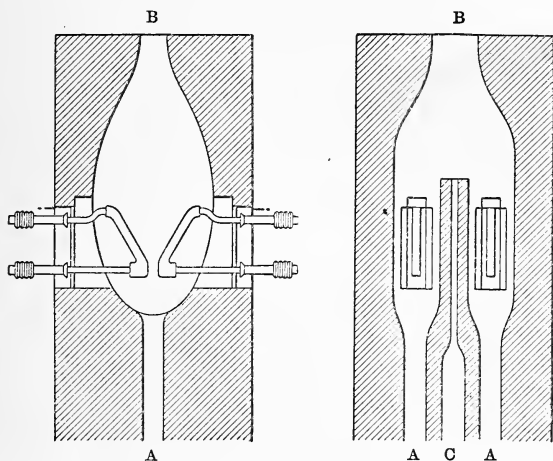


FIG 4.

returned to the furnaces for cooling purposes, and the rest is sent to the absorption towers, which are arranged on the same principle as that described under the Birkeland-Eyde process. The great dilution of the oxides of nitrogen necessitates a very large absorption system. There are five acid towers, giving finally about 25 per cent.  $\text{HNO}_3$ . The last traces of oxides of nitrogen are absorbed by  $\text{Na}_2\text{CO}_3$  or  $\text{NaOH}$  in four alkali towers, and the solution

obtained gives on concentration nearly pure  $\text{NaNO}_2$ . The yield by the Pauling process is said to be about 75 grams  $\text{HNO}_3$  per K.W.H. Furnaces with 400 and 600 kilowatt capacity are in operation. The Pauling process is in operation in Austria, Italy, and France.

**The Schönherr Process.**<sup>73</sup>—In 1905 Schönherr, of the Badische Anilin- und Soda-Fabrik, with the co-operation of the engineer Hessberger, succeeded in devising a furnace of very simple construction. He found that a stable arc of great length could be maintained in the axis of a tube along which a current of air is passed. The stability of the arc is increased by imparting to the air a whirling motion, so that in their passage along the tube the air particles follow a spiral path. The principle of the furnace differs from that of the two types just described, in which the air current is introduced at right angles to the direction of the discharge, so as to give short contact with the heated area. In the Schönherr furnace the air current passes along the arc and surrounds it, and is thus in contact with the arc for an appreciable time. In spite of this the concentration of NO in the furnace gases is higher than in either of the other two types of furnace—a result which is explicable by the electrical theory of NO formation. The construction of the furnace is shown diagrammatically in Fig. 5. One electrode is insulated from the rest of the furnace, and consists of a water-cooled copper block through which passes an iron rod E. This rod forms the actual electrode from which the arc starts, and as it wears away can be pushed

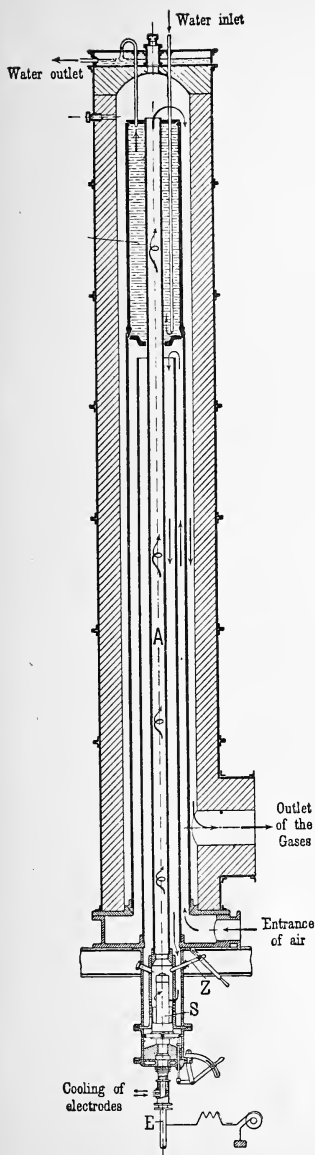


FIG. 5.

up. The inner iron tube A forms the actual reaction chamber, and is surrounded by a series of concentric tubes by means of which the entering air is preheated by the hot gases leaving the furnace. The path of the air is evident from the figure. The reaction tube forms the second electrode, and is earthed to prevent danger to the operator. The air is admitted to the reaction chamber by a series of rows of tangential openings at the bottom of the tube. A rotary motion is thus imparted to the air current. The admission of air can be regulated by a movable sleeve by means of which the number of openings can be varied. The arc is started by bringing an iron bar, actuated by the lever Z, in momentary contact with the electrode E. The arc is then carried up the tube by the air current, and by suitable manipulation of the air-regulating valve is made to end on the upper

water-cooled part of the reaction chamber. In the technical furnaces arcs up to 21 ft. long are employed. The wear of the apparatus is exceedingly slight. The iron electrode E must be renewed about four times a year. This is rapidly done by screwing a new rod to the end of the old one. The wear of the cooler, where the arc ends, is also slight, as the end of the arc is continually changing its position, so that no part gets overheated. The cooler is also so constructed that it can be readily replaced. A constant interchange of gases between the intensely hot layer next the arc and the outer cooler layer is brought about by diffusion and eddy currents. The NO formed is thus rapidly cooled and preserved. The gases leaving the reaction chamber have a temperature of about  $1200^{\circ}$ , which is reduced to about  $850^{\circ}$  by preheating the entering gases. They contain 2-2.5 per cent. NO. The heat of the gases leaving the furnace is utilised in much the same way as in the Birkeland-Eyde process for evaporating solutions, heating water, and raising steam. Schönherr states that of the total energy supplied about 40 per cent. appears as hot water, and 30 per cent. as steam; 17 per cent. is lost by radiation, and 10 per cent. by cooling with water. Only about 3 per cent. is actually used in the production of NO. Similar figures probably apply to the Birkeland-Eyde and Pauling processes. The yield is about 70 grams  $\text{HNO}_3$  per K.W.H. The capacity of the furnaces in use varies from 440-800 kilowatts.

At the Christiansand factory the furnace gases are cooled to about  $300^{\circ}\text{C.}$ , when they contain approxi-

mately equimolecular proportions of NO and NO<sub>2</sub>. By absorption with hot NaOH they give practically pure NaNO<sub>2</sub>. In the other factories the NO is transformed into HNO<sub>3</sub> in much the same way as described under the Birkeland-Eyde process. The Birkeland-Eyde and Schönherr interests are now combined, and several large factories are in operation in various parts of the Scandinavian peninsula.

For the concentration of the dilute HNO<sub>3</sub> obtained from the absorption towers various methods have been proposed.<sup>74</sup> It may be concentrated to about 50 per cent. by the waste heat from the furnace gases. If concentrated nitric acid is required, this dilute acid is distilled with concentrated sulphuric acid; the dilute sulphuric acid remaining is re-concentrated and used again. An electrolytic method of concentration has also been proposed by Pauling,<sup>75</sup> but does not appear to be in use.

An exhaustive account of the utilisation of Scandinavian water-power in the air-nitrate industry, and of its financial and commercial organisation, is given by Norton.<sup>4</sup>

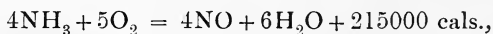
**Synthesis of Nitric Oxide by Non-electrical Means.**—It has already been pointed out that small quantities of oxides of nitrogen are produced by the explosion of such gases as carbon monoxide<sup>150</sup> or hydrogen<sup>151</sup> with air, or by their combustion in air, especially under pressure. Various methods<sup>152</sup> based on these or similar reactions have been proposed for the production of nitric acid from air. Whilst some of them are quite sound in principle, none of them has so far met with any measure of technical success.

**Oxidation of Ammonia to Nitric Acid and Nitrous Acid.**<sup>76</sup>—The development of nitrogen fixation processes during the last ten years, and especially during the war, has shown that the most generally applicable processes are those in which the final product is ammonia, such as the cyanamide (p. 98), the Haber (p. 69), and possibly the cyanide process (p. 97). The arc process depends to a much greater extent than the others on cheap electrical energy, and will probably be confined to districts where water-power is abundant and cheap.

If nitric acid is required, the ammonia must be oxidised to nitric acid. A great many methods for effecting the oxidation have been proposed.<sup>77</sup> Here, however, we need consider only the oxidation by atmospheric oxygen in the presence of catalytic agents.

Kuhlmann<sup>78</sup> first found that a mixture of air and ammonia, when passed over heated spongy platinum, gave oxides of nitrogen, but it is only in recent years that the conditions for the best yield have been more or less thoroughly investigated.

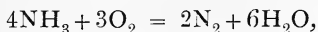
The main reaction which takes place during the oxidation of ammonia in presence of platinum is the production of nitric oxide,



although various other reactions may occur simultaneously to a greater or less extent, according to the conditions. The theoretical yield of nitric oxide is never obtained. Some of the nitrogen of the ammonia always appears as free nitrogen, probably



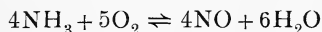
formed mainly by the subsequent decomposition of the nitric oxide, although a direct oxidation of ammonia to nitrogen and water,



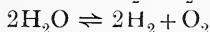
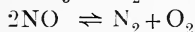
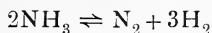
and a reaction between nitric oxide and ammonia may take place to some extent,



If it is assumed that the reaction



is reversible, it can be shown from the known values of the equilibrium-constants of the reactions—



that even at high temperatures (up to  $1000^\circ$ ) the conversion of ammonia into nitric oxide is practically complete. The application of Nernst's theorem to the ammonia oxidation equilibrium leads to the same conclusion,<sup>160</sup> and this agrees with the result found in practice that the yield of nitric oxide is practically independent of the temperature up to about  $1000^\circ$ . Above this temperature the secondary decomposition of nitric oxide becomes appreciable.

Ostwald and Brauer<sup>79</sup> studied the catalytic oxidation with a view to its technical application, and evolved an apparatus which was in use up to the end of the war, but which is being displaced by more modern plant. The catalyst used by Ostwald was platinum foil with a certain proportion of spongy

platinum on its surface, but in modern practice this has been replaced by platinum gauze.

Using platinum gauze as catalyst it is possible to get and maintain a conversion of about 95 per cent. of the ammonia into nitric oxide. The reaction is accompanied by a very considerable evolution of heat, and with an apparatus of the proper dimensions and design it is possible to maintain the platinum at 650-700° C., the usual working temperature, without the aid of external heating. Higher working temperatures have been recommended, up to 1000° C., in which case it is necessary either to heat the platinum gauze electrically, or to pre-heat the air by the hot reaction products in a heat exchanger. The time of contact of the gases with the catalyst is of the order of a thousandth of a second, but may be considerably greater without any serious diminution in efficiency. The composition of the air-ammonia mixture has also remarkably little effect on the efficiency of conversion.

Theoretically we require for

NO, 5.95 vols. air for 1 vol. $\text{NH}_3$ , or 14.4% $\text{NH}_3$ by vol.					
$\text{N}_2\text{O}_3$ , 7.14	„	„	„	12.3%	„
$\text{NO}_2$ , 8.33	„	„	„	10.7%	„
$\text{N}_2\text{O}_5$ , 9.52	„	„	„	9.5%	„

The usual working composition of the air-ammonia mixture is about 10-11 per cent.

The effect of impurities<sup>161</sup> in the gas varies with the nature of the substance. Dust, especially metallic oxides, such as iron oxide, must be rigidly excluded, as it destroys the activity of the platinum; moisture

in the gas has practically no effect, and traces of hydrogen sulphide, cyanogen, and pyridine, such as occur in purified 25 per cent. ammonia from gas liquor, have also no appreciable influence. Traces of hydrides of phosphorus, such as might occur in ammonia from cyanamide, have a marked effect. Two to three parts of  $\text{PH}_3$  per 100 million of gas mixture diminish the yield by several units per cent., and 20-30 parts per 100 million are ruinous.

The platinum does not at once attain its full activity. This is reached slowly, after the platinum has been in use for some hours. The bright platinum gradually assumes a grey colour, and the surface becomes spongy. The physical condition of the platinum is obviously altered.

A technical plant for the oxidation of ammonia to nitric acid consists of a plant for generating ammonia, a fan or blower for the necessary air supply, the catalyst chamber or converter, in which the oxidation of ammonia to nitric oxide takes place, a set of coolers for cooling the hot gases leaving the catalyst, and a series of towers in which the absorption of the oxides of nitrogen and their oxidation to nitric acid take place.<sup>162</sup> The absorption system is similar to that used in the arc process.

The ammonia supply may be obtained from purified 25 per cent. ammonia liquor, which is treated in the ordinary way in a column still with steam or steam and air. By regulating the feed of ammonia to the still a steady stream of ammonia gas is obtained. Ammonia from the Haber process or from the hydrolysis of calcium cyanamide may also be

employed. In the latter case it should be scrubbed with a concentrated solution of caustic soda to remove phosphorus compounds especially. The ammonia is mixed with a supply of air from a fan or blower, necessary to give the required air-ammonia mixture—say 10 per cent. ammonia. The mixing takes place in a large box provided with baffles. The air and ammonia are metered and the composition of the mixture is controlled by frequent analyses. The air-ammonia mixture is then filtered through cotton- or slag-wool and led to the converter. Up to this point the gas mains are of cast iron, but between the filter and the converter the gas should not come in contact with iron, and stoneware, silica, or aluminium pipes are used in this part of the path.

Various types of converter are used. In the original Ostwald apparatus the converter consisted of two concentric tubes, the inner of nickel, about 8 feet long and two inches diameter, and having a plug of platinum foil about 2 cms. thick at the upper end. The platinum weighs about 50 grams. The outer jacket is of enamelled iron. The air-ammonia mixture passes up the outer jacket, through the platinum plug, and down the nickel tube to the main carrying the gases to the absorption system. The air-ammonia mixture passing up the outer tube is pre-heated by the hot gases descending the nickel tube. Such a unit is said to produce about 30 tons of nitric acid per annum or about 0.6 ton per gram of platinum. A plant consists of a battery of such units. The main drawbacks to such

a plant are the small size of the units, the large cost, the large amount of platinum required, and the difficulty of regulating the temperature of the catalyst.

The modern converters usually consist of a rectangular or circular aluminium box, built in sections, with baffles below to give thorough mixing of the air and ammonia before the mixture reaches the catalyst. The latter is of platinum mesh, usually woven of wire 0.0026 inch in diameter and 80 meshes to the inch. The net stretches completely across the box, being clamped between two sections. More than one net—up to three or four—may be used. They are placed close together, and, if necessary, may be heated electrically. The air-ammonia mixture may be pre-heated before reaching the gauze, and the heat of the reaction may be utilised for this purpose by using a heat exchanger. The experimental evidence all points to such pre-heating being advantageous. To start the reaction the gauze is heated either electrically or by a Bunsen flame introduced through an opening in the aluminium box, which can be subsequently closed. The reaction starts at the heated area and gradually spreads over the whole net; when fully activated, the whole area of the platinum gauze glows with a red heat, and the reaction goes continuously. A convenient size of catalyst is 1 foot by 1 foot, although both larger and smaller areas of gauze are employed. The catalyst chamber is provided with a mica window for inspecting the gauze, and the aluminium exit pipe from the chamber has an opening by which

samples of the exit gases may be withdrawn for analysis.

The hot gases from the converter are led through a heat exchanger and a series of water cooled tubes. Here the steam condenses. The water formed dissolves remarkably little oxides of nitrogen, the condensate being only weakly acid. The oxidation of the nitric oxide to nitrogen peroxide begins as soon as the gases leave the converter, but cannot be complete until the temperature falls to about  $140^{\circ}\text{C}$ . The gases, cooled to about  $30^{\circ}\text{C}$ ., are then led to the series of absorption towers. The air necessary to complete the oxidation of the nitric oxide to nitric acid is added here. In their passage up the packed absorption towers the mixed oxides of nitrogen and air meet with a descending stream of water or dilute nitric acid from the next tower and are converted to nitric acid as in the arc process, except that a more concentrated acid is obtained, as the gas contains about 10 per cent. of nitric oxide, compared with 1-2 per cent. in the arc process.

The use of these converters with platinum gauze catalyst has the advantage over the Ostwald type of greater ease of regulation, larger units, smaller initial cost, and a very much greater yield of nitric acid per gram of platinum in the same time.

The only catalyst which has been used on a technical scale, so far as one can learn, is platinum, although an efficiency equal to that of platinum is claimed for numerous other catalysts. Thus many metallic oxides or mixtures of metallic oxides, such

as burnt pyrites, thorium oxide, or mixtures of this with other rare earth oxides, have been patented as catalysts or have been investigated experimentally,<sup>80</sup> and many metals, especially iron alloyed with varying quantities of other metals which act as "promoters" of its activity (Ce, Bi, Th, W, Cu), have been proposed in place of platinum.<sup>81</sup> Although some of these oxides are undoubtedly effective catalysts, large quantities of them are usually required compared with platinum. This leads to a complication of the plant, and in spite of their cheapness, it is doubtful if they will displace platinum.

**Oxidation by Nitrifying Bacteria.**—Interesting results have been obtained by Müntz and Lainé<sup>82</sup> in their endeavours to utilise nitrifying bacteria for the oxidation of ammonia to nitric acid on a large scale. They find that the best medium is peat. This is impregnated with sufficient lime to combine with the nitric acid formed, and inoculated with the bacteria. A dilute solution of  $(\text{NH}_4)_2\text{SO}_4$  (0.75 per cent.) is allowed to trickle through the mass, and a nearly 1 per cent. solution of  $\text{Ca}(\text{NO}_3)_2$  is obtained. Only dilute solutions of  $(\text{NH}_4)_2\text{SO}_4$  undergo quick nitrification, but as the presence of even 22 per cent. nitrate in the solution does not interfere with nitrification, more  $(\text{NH}_4)_2\text{SO}_4$  can be added to the dilute nitrate solution, which can then be again subjected to the action of the bacteria. Proceeding in this way, Müntz and Lainé obtained a solution containing 41.7 grams nitrate per litre by passing the solution five times through the peat, and even then the limit was not reached. The most favourable temperature is

30° C. The yield obtained was 6·5 kilos. of calcium nitrate in twenty-four hours per cubic metre of peat, compared with about 5 kilos. of crude saltpetre in two years per cubic metre of the old "saltpetre plantations."



## SECTION II.

### SYNTHESIS OF AMMONIA AND AMMONIUM COMPOUNDS FROM ATMOSPHERIC NITROGEN.

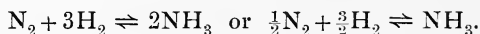
**The Equilibrium between Nitrogen, Hydrogen, and Ammonia.**—It has long been known that ammonia, which is quite stable at ordinary temperature, breaks up into its elements on heating. Thus Priestley observed the decomposition of the gas on passing it through a red hot glass tube. Other investigators confirmed the decomposition, but obtained very varying results as to the degree of decomposition, which was found to depend largely on the nature and extent of the surface in contact with the gas. The catalytic effect of different substances and the influence of a large surface of contact are well illustrated by the experiments of Ramsay and Young,<sup>83</sup> who showed that in iron or porcelain tubes, or in glass tubes filled with asbestos, the decomposition commenced at ca. 500° C. and was practically complete at 780°, whilst in glass vessels alone the decomposition did not begin until ca. 780°. They further showed that the observed degree of decomposition depended very largely on the velocity with which the  $\text{NH}_3$  was passed through the heated tube.

Ammonia is also decomposed under the influence of electric sparks, and it was generally held that

the decomposition was complete on prolonged sparking. Deville<sup>84</sup> showed, however, that even on prolonged sparking a trace of ammonia remained undecomposed, and he thus demonstrated the reversible nature of the reaction.

The reverse reaction, the synthesis of  $\text{NH}_3$  from its elements under the influence of the electric spark, was also early observed and repeatedly confirmed. The union took place only to a limited extent, unless the  $\text{NH}_3$  formed was removed, *e.g.* by combination with an acid, as fast as it was formed. A summary of the earlier work on the subject is given by Gmelin-Kraut<sup>85</sup> and by Abegg,<sup>86</sup> and, especially of the patent literature, by Rideal and Taylor.<sup>165</sup>

These facts are explained as follows. The reaction between nitrogen and hydrogen leads to an equilibrium according to the equation—



At equilibrium the following relation holds:—

$$\frac{p_{\text{NH}_3}}{p_{\text{N}_2}^{\frac{1}{2}} \times p_{\text{H}_2}^{\frac{3}{2}}} = K_p,$$

where  $p_{\text{NH}_3}$ ,  $p_{\text{N}_2}$ , and  $p_{\text{H}_2}$  are the partial pressures of  $\text{NH}_3$ ,  $\text{N}_2$ , and  $\text{H}_2$  respectively at equilibrium and  $K_p$  is the equilibrium-constant. The concentration of  $\text{NH}_3$  present at equilibrium depends on the temperature and pressure. For a given temperature and pressure the proportions of the three gases present at equilibrium should, of course, be the same, whether we start with a mixture of nitrogen and hydrogen in the proportions demanded by the equation or with pure  $\text{NH}_3$ .

The union of nitrogen and hydrogen to ammonia is an exothermic reaction, and, at ordinary temperature, is accompanied by an evolution of 11,890 cal. per gram-mol. of  $\text{NH}_3$ ; the concentration of  $\text{NH}_3$  at equilibrium must, therefore, diminish with increasing temperature. To obtain a high concentration of  $\text{NH}_3$  at equilibrium, therefore, the temperature must be kept as low as possible. On the other hand, the velocity with which the equilibrium is reached decreases with decreasing temperature, so that unless a suitable catalyst is available it may be impossible to reach the equilibrium at low temperatures.

Since the combination of nitrogen and hydrogen to  $\text{NH}_3$  is accompanied by a diminution of pressure at constant volume, increase of pressure will increase the concentration of  $\text{NH}_3$  at equilibrium for a given temperature.

The first systematic investigation of the equilibrium by modern methods was made by Haber and van Oordt.<sup>87</sup> They used iron and nickel as catalysts, and worked at ca.  $1000^\circ\text{C}$ . and at atmospheric pressure. The equilibrium was reached from both sides by the following ingenious arrangement. Pure dry  $\text{NH}_3$  was passed through a porcelain tube, which contained the catalyst, heated in an electric furnace. The  $\text{NH}_3$  was absorbed from the issuing gases by  $\text{H}_2\text{SO}_4$ , and the remaining mixture of 1 vol.  $\text{N}_2$  and 3 vols.  $\text{H}_2$  passed through another porcelain tube containing catalyst lying alongside the first in the furnace. The  $\text{NH}_3$  formed by the union of  $\text{N}_2$  and  $\text{H}_2$  in this second tube was also absorbed by  $\text{H}_2\text{SO}_4$ .

The volume of the residual nitrogen and hydrogen was measured and the  $\text{NH}_3$  formed in the two  $\text{H}_2\text{SO}_4$  flasks determined by titration. From these data the concentration of  $\text{NH}_3$  at equilibrium at the temperature of the furnace was determined. At  $1020^\circ \text{C}$ . they found 0.012 per cent. by volume  $\text{NH}_3$  at equilibrium, but they claim no great accuracy for this result. It showed, however, that at high temperatures, where the equilibrium is rapidly reached, the position of the equilibrium is very unfavourable for the technical synthesis of  $\text{NH}_3$ .

A more accurate investigation of the  $\text{NH}_3$  equilibrium was carried out by Haber and Le Rossignol.<sup>88</sup> They used iron, manganese, nickel and chromium as catalysts, but even with iron and manganese, the best catalysts, it was only above  $750^\circ \text{C}$ . that the equilibrium was reached quickly, and at this temperature the  $\text{NH}_3$  is almost completely dissociated. They worked at atmospheric pressure and retained the method employed by Haber and v. Oordt, with certain improvements in detail. The general results of Haber and v. Oordt were confirmed. The following table gives the results of the investigation :—

Temp. C.	$10^4 \times K_p$ .	Per cent. $\text{NH}_3$ at equilibrium.
1000	1.48	0.0048
930	2.00	0.0065
850	2.79	0.0091
800	3.34	0.0109
750	4.68	0.0152
700	ca. 6.8	ca. 0.0221

The concentrations of  $\text{NH}_3$  (per cent. by vol.) are for a gas mixture containing 3 vols.  $\text{H}_2$  and 1 vol.  $\text{N}_2$  at atmospheric pressure.

From the equilibrium equation (p. 70) it can be shown that the denominator, and consequently also the numerator, is a maximum when the partial pressure of  $\text{H}_2$  is three times the partial pressure of  $\text{N}_2$ , *i.e.*, when the gases are present in the proportions demanded by the equation  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$ . The maximum concentration of  $\text{NH}_3$  at equilibrium for a given temperature and pressure will, therefore, be obtained when the  $\text{H}_2$  and  $\text{N}_2$  are present in these proportions.

From the equilibrium determined at these high temperatures, the concentration of  $\text{NH}_3$  for equilibrium at lower temperatures was calculated by means of the formula—

$$\text{Log}_{10} K_p = \frac{2215}{T} - 3.626 \log_{10} T + 3.07 \times 10^{-4} T + 2.9 \times 10^{-7} T^2 + 4.82,$$

which takes into account the variation of the heat of the reaction with temperature. At  $327^\circ \text{C}$ . the equilibrium mixture should contain 1.67 per cent.  $\text{NH}_3$ , and at  $27^\circ \text{C}$ . 96.32 per cent.  $\text{NH}_3$ . It is, therefore, evident that a good yield of  $\text{NH}_3$  could be obtained at low temperatures if a suitable catalyst were found.

Nernst,<sup>89</sup> from theoretical considerations, and Jost,<sup>90</sup> from the result of experiments on the  $\text{NH}_3$  equilibrium carried out under pressures up to 70 atmos., conclude that the equilibrium-concentration

obtained by Haber and his co-workers are too high. They attribute the difference between their results and Haber's to the difficulty in determining the small amounts of  $\text{NH}_3$  formed under atmospheric pressure. The greater concentrations of  $\text{NH}_3$  obtained under high pressure can be much more accurately determined.

Haber and Le Rossignol,<sup>91</sup> therefore, undertook a fresh determination of the equilibrium at a total pressure of 30 atmos. They used a narrow quartz tube as reaction-chamber and Fe and Mn as catalysts, and took all precautions to eliminate errors. The equilibrium was attained from both sides, and good agreement obtained between the figures from the synthesis and the decomposition. Their results were as follows:—

Temp. C.	Per cent. $\text{NH}_3$ at equilibrium.	$10^4 \times K_p$ .
700	0.654	6.80
801	0.344	3.56
901	0.207	2.13
974	0.144 to 0.152	1.48 to 1.56

The relation between the results at 30 atmos. and at 1 atmos. can be deduced as follows:—If  $P$  is the total pressure, and  $c$  is the fraction which each gas forms of the total volume at equilibrium, then—

$$P \times c_{\text{NH}_3} = p_{\text{NH}_3}, \quad P \times c_{\text{N}_2} = p_{\text{N}_2}, \quad P \times c_{\text{H}_2} = p_{\text{H}_2},$$

and we get from the equilibrium equation (p. 70)—

$$\frac{c_{\text{NH}_3}}{c_{\text{N}_2}^{\frac{1}{2}} \times c_{\text{H}_2}^{\frac{3}{2}}} = K_p \times P.$$

So long as the  $\text{NH}_3$  concentrations are small, which is the case in the temperature interval investigated both at 1 atmos. and at 30 atmos., the product  $C_{\text{N}_2}^{\frac{1}{2}} \times C_{\text{H}_2}^{\frac{3}{2}}$  will be practically constant. In this case it is evident from the above equation that, for a given temperature, the  $\text{NH}_3$  concentration at equilibrium will be proportional to the total pressure.  $\text{NH}_3$  concentrations at 1 atmos. should be, therefore, about  $\frac{1}{30}$  of those at 30 atmos. for the same temperature. On this assumption the agreement between the results at 30 atmos. and the previous results at 1 atmos. is excellent. A considerable amount of further work has been done on the ammonia synthesis, both at ordinary pressure and at higher pressures, by Haber and his collaborators,<sup>166</sup> which has confirmed the results of the earlier work. In these later experiments, more efficient catalysts, such as osmium and uranium carbide, have been used.

Maxted<sup>164</sup> points out that, whilst at moderate temperatures, such as are used in the catalytic synthesis of ammonia, an increase of temperature leads to a rapid decrease in the amount of ammonia at equilibrium, when the expression given on p. 73 is used to extrapolate the equilibrium conditions at higher temperatures, the amount of ammonia at equilibrium passes through a minimum and then rapidly increases with temperature. Using the formula on p. 73, for example, the following values of  $K_p$  are calculated—

Temp. (abs.)	1000.	2000.	3000.	4000.
$K_p \times 10^4$	5.7	0.78	3.03	152.0

Maxted showed that by passing a mixture of nitrogen and hydrogen in the proportion of 1:3 through the oxyhydrogen flame and suddenly cooling the issuing gases by contact with water, yields of ammonia up to 1.23 per cent. by volume could be obtained at atmospheric pressure. Such a yield is only possible otherwise below  $350^{\circ}\text{C}$ ., a temperature at which the formation of ammonia even in presence of catalysts does not proceed with measurable velocity. Similar results were obtained by passing the mixture of nitrogen and hydrogen through a small high-tension arc. No technical application of these results has yet been made.

**Technical Synthesis of Ammonia.**—Haber and Le Rossignol next took up the question of the technical synthesis of  $\text{NH}_3$  and, with the co-operation of the Badische Anilin- und Soda-Fabrik, succeeded in devising a process which seems to offer a satisfactory solution of the problem. A short account of the experimental apparatus used is given by Haber,<sup>92</sup> and a detailed account of the apparatus, and of experiments with various catalysts by Haber and Le Rossignol.<sup>93</sup> We may here summarise the conditions most favourable for the technical synthesis of  $\text{NH}_3$ , as deduced from the investigations just discussed. The most favourable mixture of  $\text{N}_2$  and  $\text{H}_2$  is 1 vol.  $\text{N}_2$  to 3 vols.  $\text{H}_2$ . With this mixture the maximum concentration of  $\text{NH}_3$  attainable is greater the lower the temperature, whilst for a given temperature the equilibrium concentration of  $\text{NH}_3$  is higher the higher the total pressure. This is illustrated by the following table, which gives the



calculated percentage by volume of  $\text{NH}_3$  at equilibrium for different temperatures and pressures:—

Temp. C.	1 atm.	100 atm.	200 atm.
500	0.13	10.7	18.1
550		7.0	12.2
600	0.048	4.5	8.3
650		3.0	5.8
700	0.021	2.1	4.1

The lower the temperature, however, the smaller is the velocity of the reaction, and, therefore, the longer the time required for equilibrium to be reached. But in a technical process not only the concentration of  $\text{NH}_3$  attainable, but also the time taken to attain it, must be considered. The most active catalyst for the reaction must, therefore, be found, so as to enable the reaction to be carried out sufficiently rapidly at as low a temperature as possible.

Haber and Le Rossignol find that with the best catalysts at present known it is difficult to work below  $500^\circ\text{C}$ . On the other hand, it is unnecessary to go above  $700^\circ\text{C}$ ., since with these catalysts the equilibrium is practically reached at this temperature, even when the velocity of passage of the gases over the catalyst is considerable.

In their work on the technical synthesis of  $\text{NH}_3$ , Haber and Le Rossignol used pressures up to 200 atmos. The difficulties in constructing apparatus, and especially a reaction-chamber to withstand such pressures at the temperatures employed, were great, but were brilliantly overcome. Various experimental furnaces were used, according to the temperature and

pressure employed. For lower temperatures ( $500^{\circ}$ - $600^{\circ}$ ) a very simple furnace could be used. It consisted of a strong steel cylinder containing the catalyser, tightly closed with a cap. The cap

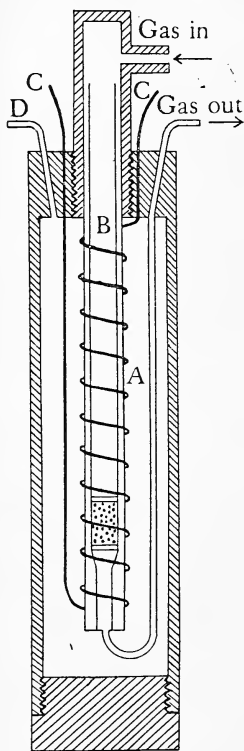


FIG. 6.

was provided with a steel capillary inlet-tube for the gases, reaching to the bottom of the cylinder, and a steel capillary exit-tube. The heating was external. For higher temperatures, above  $700^{\circ}$ , the use of metal vessels which have to stand a high internal pressure is doubtful. Fig. 6 shows diagrammatically the essential principles in the design of the furnaces for such temperatures, although several furnaces varying in details of construction were employed. The reaction-chamber consists of a thin iron tube A wrapped in asbestos and wound with nickelin wire C as heating resistance. Into the iron tube passes a glass or quartz tube B, which

is narrowed towards the lower end and contains the catalyst between asbestos plugs at this point. The gases enter the glass tube and leave at the bottom of the iron tube. The heated thin-walled iron tube would not stand a pressure of 100-200 atmos. without

deformation, unless the external pressure were also kept high. It is, therefore, surrounded by a much stronger steel tube, and a high pressure maintained in the space between the two by means of the auxiliary pressure-tube D. The space between the inner and outer tubes is filled with heat-insulating material. The arrows show the direction in which the gas passes. In the larger furnaces the hot gases leaving the reaction-chamber are, by suitable arrangements, made to give up their heat to the fresh gases entering the apparatus.

With such furnaces the effect of various catalysts was investigated under varying pressures, and with varying velocity of passage of the gases. The  $\text{N}_2\text{-H}_2$  mixture (1:3) was freed from oxygen and moisture and passed through the furnace, the temperature of which was determined by thermocouples in the inner tube. The greater part of the  $\text{NH}_3$  in the gas issuing from the furnace was liquefied and measured in a suitable condensing tube. The gas leaving the condensing tube still contained some  $\text{NH}_3$  (the amount depending on the temperature of the liquefying chamber), which was determined either by a gas-interferometer<sup>24</sup> or by titration. Of the catalysts tried, namely Ce, Mn, W, Ur, Ru, Os, by far the most effective were Os and Ur. It is noticeable that in both the Fe and Cr groups, the metals of highest atomic weight are far more effective catalysts than those of lower atomic weight. The world's supply of Os is so small, however, as to preclude its use in technical work. With Ur the following results were obtained. At 600° C. and 190

atmos., with a gas velocity of 20 litres per hour, the gas contained 5·8 per cent.  $\text{NH}_3$ . At  $580^\circ\text{C}$ ., 190 atmos. and 3 litres per hour, over 7 per cent.  $\text{NH}_3$ . At  $580^\circ\text{C}$ ., 120 atmos. and 3 litres per hour, 4·8 per cent.  $\text{NH}_3$ ; 20 litres per hour, 3·5 per cent.  $\text{NH}_3$ . At  $610^\circ\text{C}$ ., 155 atmos., 3·80 per cent., 5·05 per cent., and 5·50 per cent.  $\text{NH}_3$  was obtained, with velocities of 10, 5, and 3 litres per hour respectively. At 117 atmos., 9·1 per cent.  $\text{NH}_3$  was obtained with 9·5 litres per hour at  $490^\circ\text{C}$ ., 11 per cent.  $\text{NH}_3$  with 2 litres per hour at  $508^\circ$ , and 11·9 per cent.  $\text{NH}_3$  with 2 litres per hour at  $493^\circ$ . These are lower than the equilibrium-concentrations, as the velocity was too great to allow equilibrium to be reached. From the table (p. 77) it will be seen that in no case is the concentration of  $\text{NH}_3$  so high that it would pay simply to absorb the  $\text{NH}_3$  from the reaction products and allow the residue to go to waste. A continuous process must, therefore, be adopted. The  $\text{NH}_3$  formed by the passage of the gases over the catalyst must be removed and the uncombined gases again subjected to the action of the catalyst, after the addition of fresh  $\text{N}_2$  and  $\text{H}_2$  to replace that removed as  $\text{NH}_3$ , as it is advantageous to keep up the pressure. Under the high pressure employed, the removal of the  $\text{NH}_3$  by condensation at a low temperature is a particularly simple process. For this purpose temperatures down to  $-75^\circ\text{C}$ . may be safely employed. Below this temperature there is risk of stoppage of the gas passages by solidification of the  $\text{NH}_3$ . However low the temperature used for the condensation of the  $\text{NH}_3$ , there is always some  $\text{NH}_3$  in the gases

leaving the condensing - chamber, the amount corresponding to the vapour pressure of liquid  $\text{NH}_3$  under the working conditions. This amount is higher for a given temperature in presence of a compressed foreign gas than over the pure liquid itself.

In an experiment with gas circulation to test the technical possibilities of the process the following arrangement was used. By means of a small double-acting pump the dry  $\text{N}_2\text{-H}_2$  mixture was sent through the furnace, which contained Os as catalyst. The gases leaving the furnace were dried by soda-lime and then passed through a system of copper capillaries enclosed in a strong steel cylinder, the arrangement constituting a "cold regenerator." The gases then passed to the liquefier, where the greater part of the  $\text{NH}_3$  was condensed by passing through a coil immersed in a mixture of solid  $\text{CO}_2$  and ether, which maintained a temperature of about  $-30^\circ\text{C}$ . From the liquefier the gases passed to the outer steel chamber of the "cold regenerator" and thence to the pump. In the "cold regenerator" the cold gases from the liquefier on their way to the pump are used to cool the warm gases entering the capillaries before these reach the liquefier. Between the pump and the furnace is a valve by which fresh  $\text{N}_2\text{-H}_2$  mixture is introduced to replace the  $\text{NH}_3$  removed in the liquefier. In an experiment lasting four hours the apparatus worked with extreme smoothness. With a pressure varying from 193-163 atmos., the concentration of  $\text{NH}_3$  varied from 2.4-3.1 per cent. Higher figures would have been obtained

with a larger quantity of catalyst. About 336 grams of liquid  $\text{NH}_3$  was obtained in the four hours. The heat and cold regenerators worked with surprising efficiency.

The technical synthesis of  $\text{NH}_3$  on the lines indicated by Haber has been taken up by the Badische Anilin- und Soda-Fabrik, and Bernthsen<sup>95</sup> gives a summary of the results obtained. It was found that a number of substances, such as alkali, alkaline earth, and earth oxides, hydroxides and salts, and many metals, have the power of rendering catalysts in general more active. Metals such as Pb, Zn, Sn, Bi, and metalloids such as S, Se, Te, As, B, and P must be avoided, as they act as contact poisons. Mo and many of its compounds are excellent catalysts. Another suitable catalyst is tungsten, either as metal, alloy, or nitrogen compound.

The catalyst used in the plant erected in Germany is probably a specially prepared iron catalyst containing a promoter such as molybdenum or alkali metals.

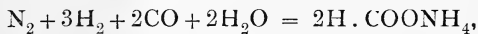
Very little has been published on the technical synthesis of ammonia. Tour<sup>167</sup> gives a short account of the American Government experimental plant.

G. Claude<sup>169</sup> claims to have shown that the use of pressures up to 1000 atm. is practicable in technical work, and has studied the synthesis of ammonia at this pressure. At  $600^\circ\text{C}$ . with the usual catalyst, 6 grams of ammonia at a concentration of 25 per cent. is got per gram of catalyst per hour compared with 0.5 gram at a concentration of 6 per cent. by

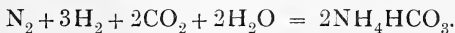
the process employed by the Badische Anilin- und Soda-Fabrik. The employment of such a high pressure permits the use of smaller catalyst chambers and a considerable reduction in the number of times the gas mixture must be passed over the catalyst, whilst the partial pressure of ammonia in the mixture is such that simple cooling with water is sufficient to liquefy the greater part of it.

A great advantage of the  $\text{NH}_3$  synthesis for the fixation of nitrogen is that the amount of energy required for the process is small. The manufacture of synthetic ammonia would not, therefore, be confined to districts where large amounts of cheap water-power are available, as is the case with the manufacture of nitric acid or of calcium cyanamide from atmospheric nitrogen.

**Various Processes for Ammonia and Ammonium Compounds.**—Of the numerous other methods which have been from time to time proposed for the conversion of atmospheric nitrogen into ammonia or ammonium compounds, the following may be mentioned. According to De Lambilly,<sup>96</sup> a mixture of nitrogen, hydrogen, steam and carbon monoxide passed over certain catalysts, especially spongy platinum, gives ammonium formate—



whilst if the CO is replaced by  $\text{CO}_2$  ammonium bicarbonate results—



Technically the gases can be obtained by the alternate action of air and steam on white-hot

coke. According as bicarbonate or formate is desired, the CO or CO<sub>2</sub> is removed from the gas mixture before subjecting it to the action of the catalyst. The most favourable temperature for the formate formation is 80°-130°, and for the bicarbonate formation 40°-60°.

Schlutius<sup>97</sup> exposes a mixture of Dowson gas (14 per cent. H<sub>2</sub>, 43 per cent. N<sub>2</sub>, 39 per cent. CO, 4 per cent. CO<sub>2</sub>) and steam to the action of the silent discharge in presence of platinum. Above 80° ammonium formate is obtained, below 80° ammonia.

For an account of various other processes the reader is referred to Donath and Indra,<sup>98</sup> or to Lunge.<sup>99</sup>

Various inventors<sup>100</sup> have patented processes for the recovery of the nitrogen in peat as ammonia, and have claimed that at the same time a synthesis of ammonia from atmospheric nitrogen takes place under the catalytic influence of the peat. In such processes a mixture of air and steam is passed over peat at 300°-500°. The reaction is capable of furnishing an excellent power-gas, together with various valuable by-products, including NH<sub>3</sub>. Caro<sup>101</sup> has shown, however, that it is not possible to obtain a yield of NH<sub>3</sub> greater than corresponds to the combined nitrogen in the peat, so that no synthesis from atmospheric nitrogen takes place. An account of the utilisation of peat for the production of power-gas, ammonia, and other by-products is given by Norton,<sup>102</sup> Donath and Indra,<sup>103</sup> and by Lunge.<sup>104</sup>

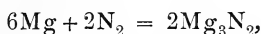


### SECTION III.

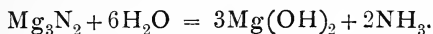
#### CONVERSION OF ATMOSPHERIC NITROGEN INTO COMPOUNDS WHICH READILY YIELD AMMONIA.

##### **Formation and Decomposition of Nitrides.**

MOST metals, and many non-metals, combine more or less readily with nitrogen to form nitrides, from most of which the nitrogen can be obtained in the form of ammonia by treatment with water or alkalies. Thus heated magnesium readily absorbs nitrogen, forming nitride—



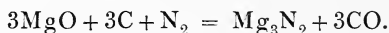
and the nitride is decomposed by water as follows:—



The metals which readily form nitrides are much too dear, however, to allow of such processes being carried out remuneratively on a technical scale. Methods were, therefore, sought by which the nitrides could be prepared from cheap compounds of the metals, or in which the metal could be used as a catalytic agent in the synthesis of ammonia, the nitride formation being an intermediate step in the process. Of the numerous processes which have been proposed, the only one which has been in technical operation is that depending on the

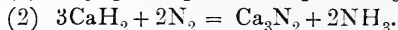
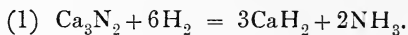
formation of aluminium nitride,  $\text{AlN}$ , although at present it seems to be no longer in operation. Of the others a few only need be mentioned here. A full account is given by Donath and Indra,<sup>105</sup> by Norton,<sup>106</sup> and by Lunge.<sup>107</sup>

Willson<sup>108</sup> and Mehner<sup>109</sup> heat a mixture of magnesia and carbon in a current of nitrogen in an electric furnace—

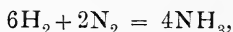


The oxides of other elements which form nitrides at high temperatures, *e.g.*, B, Si, Ti, V, etc., react similarly.

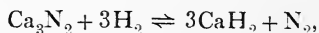
Kaiser<sup>110</sup> bases his process on the following reactions:—



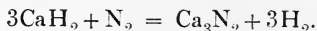
Summing these reactions we obtain—



so that a mixture of  $\text{Ca}_3\text{N}_2$  and  $\text{CaH}_2$  should act as a catalyst in the synthesis of  $\text{NH}_3$ . Haber and v. Oordt<sup>87</sup> have shown, however, that the main reaction when hydrogen is passed over heated  $\text{Ca}_3\text{N}_2$  is—



only a little  $\text{NH}_3$  being formed according to (1). When nitrogen is passed over  $\text{CaH}_2$  practically no  $\text{NH}_3$  is formed, the main reaction being—



A mixture of  $\text{Ca}_3\text{N}_2$  and  $\text{CaH}_2$ , therefore, catalyses

the synthesis of  $\text{NH}_3$  only to a slight extent, and at the temperature required (ca.  $800^\circ\text{C}.$ ) the position of the ammonia equilibrium is too unfavourable for a successful technical process. The catalysis of the  $\text{NH}_3$  synthesis by Mn, with intermediate formation of manganese nitride, is somewhat more favourable, but here also the temperature required is too high, and the intermediate action too slow.

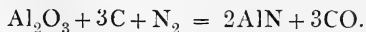
Borchers and Beck<sup>111</sup> claim to have devised a process of fairly general applicability for the conversion of compounds of many metals into nitrides from which  $\text{NH}_3$  can be prepared. A solution of a halide or oxide of the nitride-forming metal in a fused mixture of alkali or alkaline earth halogen salts is electrolysed. As cathode, a layer of molten metal is used, which does not itself form a nitride but readily alloys with the nitride-forming metal. The anodes are of carbon or resistant metal. On electrolysing, the nitride-forming metal is liberated at the cathode and alloys with the cathode metal. The fluid alloy is treated with a current of nitrogen when nitride is formed, which is removed and treated with water or steam. Ammonia is evolved and the hydroxide or oxide of the metal left. After drying, this can be returned to the electrolytic chamber. The metal acts, therefore, practically as a catalyst. The process can be used for the formation of nitrides of Al, Mg, and the alkaline earth metals.

Numerous methods depending on the transformation of oxides and other compounds of B, Si, Ti, and Mo into nitrides or other nitrogen compounds of these elements, and the subsequent decomposition of the

nitrogen compounds by water, acids, or alkalies, have been described and patented. It is, however, impossible to consider them here. An account of them will be found in the sources quoted above. None of them, so far as can be ascertained, have been tried on a technical scale.

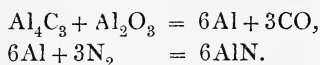
**Serpek's Aluminium Nitride Process.**—The only process depending on the formation of a metallic nitride which at present seems to offer prospects of technical success is that devised by Serpek, which depends on the production of aluminium nitride from alumina, and subsequent decomposition of the nitride. An account of the development of the process is given by Norton,<sup>112</sup> Donath and Indra,<sup>113</sup> and Richards.<sup>114</sup> Serpek at first used powdered aluminium carbide as raw material, and heated this in a current of nitrogen or generator-gas. The absorption of nitrogen was said to be increased by the addition of carbon or aluminium to the carbide, and by the presence of traces of  $\text{SO}_2$  or  $\text{HCl}$  in the gas-current. Caro<sup>115</sup> showed that the absorption of nitrogen by  $\text{Al}_4\text{C}_3$  was probably preceded by dissociation of the carbide into aluminium and carbon.

Later a mixture of alumina and carbon (coal) was heated in a current of nitrogen or generator-gas to red heat. The formation of nitride takes place according to the equation—



The addition of 5 per cent. copper or iron facilitated the absorption, and the action of these metals was

regarded as catalytic. In this case also the presence of traces of  $\text{SO}_2$  or  $\text{HCl}$  was said to favour absorption of nitrogen. Serpek assumed that  $\text{Al}_4\text{C}_3$  was first formed, which then reduced the remaining  $\text{Al}_2\text{O}_3$  to aluminium, which combined with the nitrogen—



Further investigation showed that the yield of nitride depended greatly on the temperature employed. It was found that some absorption of nitrogen took place even at  $1100^\circ\text{C}.$ ; at  $1500^\circ$  nitrogen was absorbed fairly rapidly, at  $1700^\circ$  energetically, and at  $1800^\circ$ - $1850^\circ$  almost violently, giving nearly chemically pure nitride. Smaller yields were obtained at higher temperatures, and above  $2000^\circ\text{C}.$  the production of nitride practically ceased, owing to decomposition of the nitride. The most favourable temperature is, therefore,  $1800^\circ$ - $1900^\circ$ . It was also found that impure alumina, such as bauxite, could be converted into nitride at somewhat lower temperatures than pure, evidently owing to the catalytic effect of the impurities.

The Serpek process was tested in France on a large scale by the Société Générale des Nitrures, who acquired all the Serpek patents. The apparatus used is shown diagrammatically in Fig. 7. It consists of two superposed, rotating cylindrical kilns, slightly inclined to one another and rotating in opposite directions. Into the upper one, A, the powdered bauxite is introduced and is calcined in its descent by the passage of the hot gases over it. The calcined

bauxite falls into the funnel B in the chamber D and is there mixed with the necessary carbon, introduced at P. The mixture then enters the cylinder C, and in its descent passes the electrically heated region F, where it is heated to the reacting temperature  $1800^{\circ}$ - $1900^{\circ}$ . The iron cylinder C is lined with compressed nitride. The detachable electrical resistance furnace F is formed of a series of bars

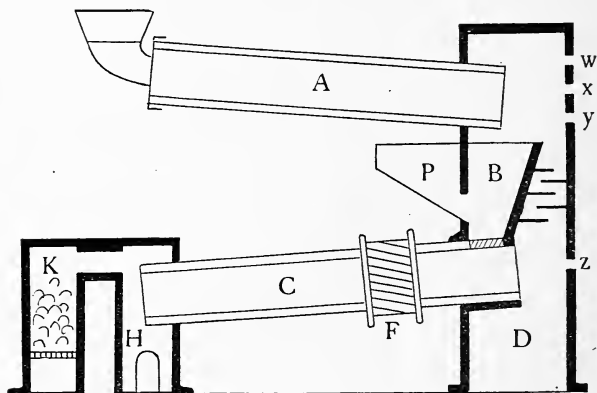
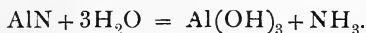


FIG. 7.

of compressed carbon and  $\text{AlN}$ . These are either embedded longitudinally in the lining of the furnace, or cross the furnace diametrically. Generator gas (ca. 30 per cent.  $\text{CO}$  + 70 per cent.  $\text{N}_2$ ) is produced in the generator K and enters C at a temperature of ca.  $400^{\circ}$ . It becomes highly heated in passing through the kiln in the direction contrary to that of the descending charge. In the electrically heated region the nitrogen reacts with the alumina-carbon mixture, giving  $\text{AlN}$  and  $\text{CO}$ . The gas, rich in carbon

monoxide, leaving the high temperature zone preheats the descending charge, issues from the upper end of the kiln into the mixing chamber D, where it meets with a blast of air from  $w, x, y, z$ , which burns the carbon monoxide to carbon dioxide. The heat produced is used to calcine and preheat the bauxite in the upper kiln. The siliceous impurities in the charge are mostly volatilised out, probably as free silicon, which is burned to silica by the air blast. The chamber D is provided with baffle-plates to remove dust from the ascending gases. The nitride formed in C is collected in the air-tight chamber H. The apparatus effects the necessary intimate mixing of the charge and intimate contact of nitrogen with the charge, and at the same time secures a very economical use of the heating current, whilst the heat of combustion of the carbon monoxide, both from the generator and from the reaction, is also utilised. The product from bauxite contains about 26 per cent.  $N_2$ , but by using pure alumina, pure  $AlN$  (34 per cent.  $N_2$ ) can be obtained.

The  $AlN$  can be decomposed by water or alkali, giving  $NH_3$ —

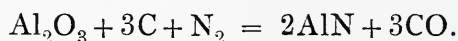


By decomposing the nitride with alkali or with sodium aluminate solution, according to the Bayer process, the nitrogen is recovered as  $NH_3$ , whilst a very pure alumina, free from iron and silica, is obtained. With  $AlN$ , too, a much more dilute alkali can be used than is possible in the manufacture of pure alumina from bauxite by the Bayer process.

The pure alumina is suitable for the production of metallic aluminium, or it may be again converted into nitride.

**Scientific Investigation of the Serpek Process.**

—Remarkably few scientific investigations of the reaction involved in the Serpek process have appeared. Tucker and Read<sup>116</sup> found that the absorption of nitrogen by a mixture of alumina and carbon was very slight below 1600° C., reached a maximum between 1800° and 2000° C., whilst above 2000° decomposition of the AlN seemed to occur. The formation of the nitride takes place according to the equation—



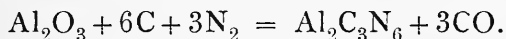
Serpek's statement that bauxite reacts more readily than pure alumina was confirmed, but it was found that the presence of appreciable amounts of SO<sub>2</sub> in the nitrogen was harmful.

An important contribution to the subject was recently made by Fraenkel,<sup>117</sup> who gives also a very complete bibliography of the earlier literature on aluminium nitride. Fraenkel studied the velocity of absorption of pure dry nitrogen by a mixture of 2 parts pure alumina and 1 part finely divided pure soot, and found that the velocity of absorption is very small at 1350° increases moderately up to 1500°, and very rapidly above 1500°. Thus in thirty minutes 0·2 per cent. N<sub>2</sub> was absorbed at 1350°, 3·1 per cent. at 1400°, 4·4 per cent. at 1450°, 8 per cent. at 1500°, 19·5 per cent. at 1550°, and 24·5 per cent. at 1600°. Up to 1500° the amount



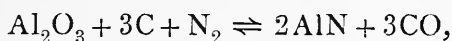
of nitrogen absorbed is approximately proportional to the time, but at higher temperatures the reaction goes quickly at first, and then, after a large proportion of the charge has reacted, slows down considerably.

According to Peacock and Du Pont<sup>118</sup> a mixture of 3 parts of alumina and 1 part of carbon reacts with nitrogen under 500 mm. pressure at 1500° according to the equation—



Fraenkel obtained no indication of such a reaction, but found that at pressures down to 250 mm. the velocity of the reaction was practically the same as at atmospheric pressure.

A different result is obtained if the partial pressure of the nitrogen is lowered by mixture with another gas, especially CO, the product of the reaction. If we regard the reaction—



as reversible, the law of mass-action gives  $C_{\text{N}_2}/C^3_{\text{CO}} = K$ . The reversibility of the reaction was proved by passing different mixtures of  $\text{N}_2$  and CO at a given temperature either over a mixture of alumina and carbon, or over a mixture containing a certain proportion of AlN, and determining the percentage of nitrogen in the mixture before and after passing the gas. When the proportion of CO in the gas mixture was above a certain amount, the percentage of nitrogen in the solid diminished, showing that

the reaction from right to left was taking place. When the proportion of CO was below a certain amount, nitride formation took place. The results show distinctly that an equilibrium exists, but it was not possible to define it accurately. At a total pressure of 1 atmos. the equilibrium concentration of CO at 1500° is between 25 per cent. and 40 per cent. CO, and at 1600° between 50 per cent. and 65 per cent. CO. At 1700° active absorption of nitrogen still took place from a gas containing 70 per cent. CO. With increasing temperature the equilibrium concentration of CO, therefore, increases. This result is important technically. If generator gas is used, a higher temperature is required than with pure nitrogen, and the higher the temperature the less pure does the nitrogen require to be. Further, with generator gas it is useless to look for catalysts for the reaction in the neighbourhood of 1500°. These can be effective only with nitrogen containing less CO than generator gas.

A shifting of the equilibrium with temperature in the direction found indicates that the reaction from left to right is endothermic. In agreement with this, Fraenkel calculated the heat of this reaction to be ca. -243000 cals., and Richards<sup>114</sup> -213220 cals. The reaction is, therefore, strongly endothermic.

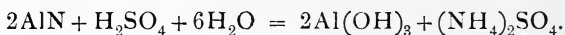
As a result of an investigation of the influence of different forms of carbon and of various catalysts on the velocity of the reaction Fraenkel states that different forms of carbon show essential differences in reaction-velocity, and that none of the catalysts so frequently mentioned in the Serpek patents

show any marked influence on the reaction-velocity in the neighbourhood of  $1500^{\circ}$ , but that the presence of alkali powerfully accelerates the formation of aluminium nitride.

The Badische Anilin- und Soda-Fabrik <sup>119</sup> has also investigated the technical production of aluminium nitride. They find that the formation of nitride from alumina and coal is greatly accelerated by the presence of 5-10 per cent. of the oxides of certain elements which themselves can form stable nitrides. Under these conditions it is possible to secure rapidly and easily a fairly high percentage of nitrogen in the product. Among the oxides which may be used are those of Si, Ti, Zr, Mo, V, Be, Ce, Ur, Cr. Preference is given to  $\text{SiO}_2$  on account of its cheapness, but under certain local conditions some of the others might be used with advantage, especially as they are recovered and can be used again. The oxides may be replaced by other oxygen compounds, such as silicates, titanates, vanadates, etc. The presence of iron and other impurities does not influence the catalytic action, so that low-grade bauxite may be employed.

The Badische <sup>120</sup> has also worked out methods of treating the crude nitride, so that, whilst the ammonia is completely recovered, the aluminium is obtained in the form of a pure compound. Thus by treating the crude aluminium nitride, containing, for example, silicon nitride, with limited amounts of acid or alkali, the aluminium may be obtained as a soluble compound, free from silica. The quantity of acid or base can also be chosen so that

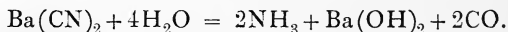
the aluminium remains as insoluble hydroxide, thus—



The elimination of ammonia by alkalies is greatly facilitated by the addition of such soluble salts as sodium chloride.

### **Production of Metallic Cyanides and Cyanamides.**

The work of Defosses,<sup>121</sup> Fownes,<sup>122</sup> and Bunsen and Playfair<sup>123</sup> showed that by the action of nitrogen on a mixture of carbon and alkali or alkaline earth hydroxides or carbonates at high temperatures cyanides were formed, from which ammonia could be obtained. Several processes<sup>124</sup> based on these reactions were tried on a technical scale, but were abandoned on account of rapid deterioration of plant and high cost of production. Thus Margueritte and Sourdeval<sup>125</sup> used barium compounds instead of potassium compounds, as the former react much more readily with nitrogen. A mixture of  $\text{N}_2$  and  $\text{CO}$ , obtained by passing air over glowing coal, was passed over a heated mixture of  $\text{BaCO}_3$ , carbon, and iron. The  $\text{Ba}(\text{CN})_2$  formed was treated with steam at ca.  $300^\circ$ , when  $\text{NH}_3$  was liberated—



The  $\text{Ba}(\text{OH})_2$  was used again in the formation of fresh cyanide. A somewhat similar process was carefully worked out by Mond,<sup>126</sup> but was also given up after trial, as it was found that  $\text{NH}_3$  could be produced more cheaply by other methods.

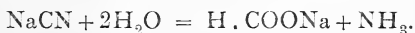
Other processes aimed at the production of technically pure cyanides from atmospheric nitrogen. Castner<sup>127</sup> passed a mixture of nitrogen and hydrocarbons over a mixture of sodium and charcoal at a red heat and obtained NaCN. It was ultimately found more economical to substitute ammonia for nitrogen, and the method at present used for the manufacture of NaCN depends on this reaction.

Recently the question of the direct production of cyanides by the action of nitrogen or producer gas on a mixture of sodium carbonate, carbon, and iron has been raised by Bucher.<sup>163</sup> He claims to have obtained practically complete conversion of the sodium carbonate into cyanide at a temperature of about 950° C. The essential part of the process is the use of metallic iron as catalyst for the reaction—



The earlier statements in the literature as to the necessity of the presence of iron were very conflicting, but Bucher has established the fact that the reaction takes place rapidly only in the presence of iron.

The cyanide can be decomposed by steam giving ammonia and a formate:—

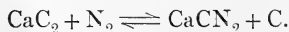


Although the reaction is extraordinarily simple, it has not yet met with any technical success, probably owing to the fact that the influence of various impurities in the mixture on the catalyst is not yet fully understood. Should the process be developed technically with no essential modifications,

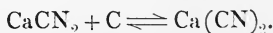
it will probably prove the cheapest for the fixation of nitrogen.

**Cyanides and Cyanamides from Carbides.**—In 1892 Moissan showed that calcium carbide,  $\text{CaC}_2$ , could be prepared easily and in quantity in the electric furnace. The technical production of  $\text{CaC}_2$  then developed rapidly, and in 1895 Frank and Caro<sup>128</sup> commenced their investigations on the absorption of nitrogen by metallic carbides, which have led to the establishment of the cyanamide industry on the present large scale. Moissan<sup>129</sup> showed that pure  $\text{CaC}_2$  did not absorb nitrogen even at  $1200^\circ$ , but Frank and Caro found that technical carbides, such as  $\text{BaC}_2$  and  $\text{CaC}_2$ , absorbed nitrogen readily at much lower temperatures, probably owing to the impurities which they contain.

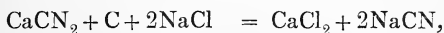
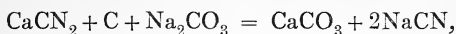
The metallic cyanamides are derivatives of cyanamide,  $\text{H}_2\text{CN}_2$ , the constitutional formula of which is generally given as  $\text{H}_2\text{N}\cdot\text{CN}$ , although in some of its reactions it behaves as  $\text{HN}=\text{C}=\text{NH}$ , carbodiimide.<sup>131</sup> The hydrogen is replaceable by metals giving the metallic cyanamides. By the action of nitrogen on metallic carbides, mixtures of metallic cyanides and cyanamides are obtained, the proportions depending on the metal and on the temperature. The general type of the reaction may be illustrated by the case of  $\text{CaC}_2$ . The formation of cyanamide takes place according to the equation—



Cyanide may then be formed as follows:—



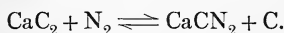
With alkali carbides, cyanide preponderates largely in the equilibrium corresponding to the second equation. With  $\text{BaC}_2$  about 30 per cent. cyanide and 70 per cent. cyanamide is obtained at  $700^\circ\text{--}800^\circ$ , whilst with  $\text{CaC}_2$  cyanamide is practically the only product up to ca.  $1100^\circ$ . The equilibrium with  $\text{SrC}_2$  lies between that of  $\text{BaC}_2$  and  $\text{CaC}_2$ . In all cases the proportion of cyanide increases with increasing temperature.<sup>128, 130, 132, 133</sup> These facts explain the formation of cyanides by fusing the mixture of  $\text{BaCN}_2$  or  $\text{CaCN}_2$  and carbon with an alkali salt, such as the carbonates or chlorides of sodium and potassium—



reactions which are used in the technical preparation of cyanides from  $\text{CaCN}_2$ .

**The Formation of Calcium Cyanamide from Calcium Carbide and Nitrogen.**—From the technical point of view the action of nitrogen on  $\text{CaC}_2$  is of the greatest importance, and although it has been the subject of numerous investigations, the exact nature of the reactions involved are not yet fully understood.

The formation of  $\text{CaCN}_2$  from  $\text{CaC}_2$  and  $\text{N}_2$  has usually been assumed to take place according to the reversible equation—



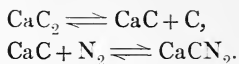
If  $\text{CaC}_2$ ,  $\text{CaCN}_2$ , and C are regarded as separate solid

phases, the system should be monovariant, and a definite equilibrium pressure of  $N_2$  should correspond to a given temperature. The attempts to measure this equilibrium pressure led to very conflicting results. Matignon<sup>134</sup> calculated on theoretical grounds, under certain assumptions, that the pressure was 1 atmos. at ca.  $1100^\circ C$ . Caro<sup>135</sup> found an equilibrium pressure of 1 atmos. at  $1360^\circ$  for a certain specimen of technical carbide. Thompson and Lombard<sup>136</sup> investigated the equilibrium between  $1050^\circ$  and  $1450^\circ C$ ., and found that the equilibrium pressure varied rectilinearly with the temperature from ca. 2.5 cms. at  $1050^\circ$  to ca. 45 cms. at  $1450^\circ$ . By extrapolation, a temperature of ca.  $1700^\circ$  is obtained for an equilibrium pressure of 1 atmos. Their equilibrium pressures, however, involve an extraordinarily rapid variation of the heat of reaction with temperature, which makes it improbable that they represent true equilibria.<sup>137</sup> Le Blanc and Eschmann<sup>138</sup> were unable to get reproducible values of the nitrogen equilibrium pressure for a given temperature, and attribute this to sublimation of the  $CaCN_2$  from hot to cold parts of the tube, where it is out of contact with carbon, and so cannot take part in the reverse reaction. Other possible disturbing factors are the gradual alteration of the carbon, so that it becomes inactive, and the occurrence of side reactions, especially with impure carbide, the effects of which could not be taken into account. From their results it appears that the system is divariant, since the equilibrium pressure seems to depend not only on the temperature, but also on the



concentration of nitrogen in the product. At  $1300^{\circ}$  this  $N_2$ -concentration is about 85 per cent., and at  $1200^{\circ}$  about 90 per cent. of the theoretical. They assume that the  $CaC_2$ - $CaCN_2$  mixture is a liquid phase, the other two phases necessary for a divariant system being solid carbon and the gas phase. The work of Erlwein, Warth, and Beutner<sup>139</sup> on the action of heat on  $CaC_2$  threw a new light on the mechanism of cyanamide formation. They found that  $CaC_2$  on heating decomposes into carbon and a lower carbide, which, although it does not react with water to give acetylene, is capable of absorbing nitrogen giving  $CaCN_2$ . A sample of technical carbide, containing 72 per cent.  $CaC_2$ , gave only about 62 per cent.  $CaC_2$  after heating for three hours at  $500^{\circ}$ - $1250^{\circ}C.$ , the  $CaC_2$ -content being practically independent of the temperature. This does not, however, represent an equilibrium, as after thirty hours at  $1000^{\circ}$  only 36.6 per cent.  $CaC_2$  remained. The addition of certain substances, especially of  $CaF_2$ , greatly accelerates the decomposition. Thus the technical carbide with 10 per cent.  $CaF_2$  contained only 27 per cent.  $CaC_2$  after three hours at  $1100^{\circ}$ , and no  $CaC_2$  after three hours at  $1260^{\circ}$ . The decomposition is especially rapid near the melting-point of  $CaF_2$  ( $1330^{\circ}$ ). Bredig, Fraenkel, and Wilke<sup>130</sup> had already found a relation between the catalytic acceleration of cyanamide formation by salt additions and the melting-point of the added salt. These decomposed carbides can still absorb nitrogen, and the view is put forward that the subcarbide is probably an intermediate step in the formation of  $CaCN_2$  from  $CaC_2$ . If the subcarbide

is assumed to be  $\text{CaC}$ , the formation of  $\text{CaCN}_2$  would take place as follows: <sup>137</sup>—



For a proper understanding of the cyanamide equilibrium a thorough knowledge of the carbide dissociation is, therefore, required, and this is at present lacking. This may account for the failure hitherto to obtain concordant results.

The rate of absorption of nitrogen by  $\text{CaC}_2$  alone, or with the addition of various substances, has been the subject of numerous investigations. Many of these have been prompted by the publication of patented processes, which claim that the addition of various substances to  $\text{CaC}_2$  greatly accelerates the absorption of nitrogen, and allows it to take place at a lower temperature. The most important of these additions are  $\text{CaCl}_2$ , proposed by Polzenius,<sup>140</sup> and  $\text{CaF}_2$ , proposed by Carlson.<sup>141</sup> Various explanations of the action of these salts have been put forward in the patent literature and elsewhere.<sup>142</sup> These explanatory hypotheses have been tested by Bredig, Fraenkel, and Wilke.<sup>143</sup> They heated powdered carbide (81.5 per cent.  $\text{CaC}_2$ ), with or without the addition of 10 per cent. of other substances, for two hours in a nitrogen atmosphere, and determined the amount of nitrogen absorbed. At  $800^\circ$   $\text{CaC}_2$  alone absorbed ca. 3 per cent.  $\text{N}_2$ ;  $\text{CaC}_2$  with 10 per cent.  $\text{CaCl}_2$  absorbed 22 per cent.  $\text{N}_2$ ; with 10 per cent.  $\text{BaCl}_2$ , 12.5 per cent.  $\text{N}_2$ ; with 10 per cent.  $\text{LiCl}$ ,  $\text{NaCl}$ , and  $\text{KCl}$ , 17 per cent., 12 per cent., and 11 per

cent.  $N_2$  respectively. It appears, therefore, that with the chlorides of metals of the same group of the periodic system the acceleration is greater the lower the atomic weight of the metal. This was confirmed with the chlorides of Be, Mg, and Sr. On the other hand, the quantity of cyanide in the product increases with the atomic weight of the metal, but at the temperatures employed is always very small with  $CaC_2$ . Addition of 10 per cent.  $CaF_2$ ,  $CaSO_4$ ,  $CaO$ ,  $Ca(OH)_2$ ,  $MgO$ , coke-powder, and sand caused little or no acceleration at  $800^\circ$ . Similar results were obtained at  $700^\circ$ , but  $LiCl$  gave a greater acceleration than  $CaCl_2$ . With  $CaC_2$  alone the absorption begins at  $750^\circ$ , whilst the mixtures with  $NaCl$  and  $CaCl_2$  begin to absorb at  $650^\circ$ . At  $800^\circ$  the initial velocity of absorption is very rapid with  $NaCl$  and  $KCl$ , but falls off much more quickly than with  $CaCl_2$ . Metallic Ca, Mg, and Na do not appreciably accelerate the velocity of absorption. From these results Bredig, Fraenkel, and Wilke exclude the following hypotheses: (1) that the real catalysers are oxysalts, since  $CaO$  cannot replace  $CaCl_2$  in efficiency; (2) that the added salt causes only a considerable initial rise of temperature, since  $CaCl_2$  shows marked catalytic effect although the temperature is kept constant; (3) that the addition serves only to make the mass more porous, since sand,  $MgO$ , and charcoal have practically no influence; (4) that the addition gives rise to dissociation products, such as Ca, which facilitate the reaction, possibly by intermediate reactions, since the addition of metallic Ca has no effect.

The other explanation is that the addition acts as a solvent in which the reaction between  $\text{CaC}_2$  and  $\text{N}_2$  goes faster than with solid  $\text{CaC}_2$ . The flux also keeps the surface of the carbide free from lime and from reaction products. Bredig, Fraenkel, and Wilke support the view that the acceleration is connected with the fusibility of the added salt, and the solubility of  $\text{CaC}_2$  in the flux. The melting-point of the salt is not, however, the only factor. The acceleration will depend on the complete melting-point diagram of the complex reaction mixture, on the solubility of  $\text{CaC}_2$  in the melt, and on the specific velocity-constant for the particular melt. They found, further, that the velocity of absorption of nitrogen is proportional to the pressure in the interval investigated (up to 1 atmos.). Rudolphi<sup>144</sup> obtained similar results with  $\text{CaCl}_2$ , and concluded that the influence of the added salt is directly connected with its melting-point, but he could not settle the exact mode of action of the fused salt. He further showed that the formation of  $\text{CaCN}_2$  from  $\text{CaO}$ ,  $\text{C}$ , and  $\text{N}_2$  begins between  $1738^\circ$  and  $1753^\circ$ , and that the formation of  $\text{CaC}_2$  precedes that of  $\text{CaCN}_2$ , since the product contains either both  $\text{CaC}_2$  and  $\text{CaCN}_2$  or neither, according as the temperature is above or below  $1738^\circ$ - $1753^\circ$ .

Foerster and Jacoby<sup>145</sup> found, in agreement with Frank and Caro, that powdered commercial carbide (containing ca. 10 per cent.  $\text{Ca(OH)}_2$ ) does not show rapid absorption of nitrogen below  $1000^\circ$ . At  $1050^\circ$ - $1100^\circ$  the absorption was rapid and complete. At lower temperatures not only is the absorption less rapid, but it is also incomplete. The amount absorbed

tends to a limiting value below the theoretically possible, and the limiting value is lower the lower the temperature. That we are not dealing here with an equilibrium is shown by the fact that the exothermic reaction is favoured by rise of temperature. A completely azotised product, prepared at  $1100^{\circ}$ , also showed no diminution of  $N_2$ -content when heated four hours at  $900^{\circ}$ . With  $CaC_2$  containing  $CaCl_2$  or  $CaF_2$  the results are different; the absorption is much more rapid than with  $CaC_2$  alone, and does not cease at a limiting value, but increases regularly with the time of heating. Thus  $CaC_2$  with 15 per cent.  $CaCl_2$  absorbed seven times as much  $N_2$  in two hours at  $700^{\circ}$  as did  $CaC_2$  alone at  $800^{\circ}$ .  $CaF_2$  requires a higher temperature than  $CaCl_2$  to show the same effect. Thus with 10 per cent.  $CaF_2$  the absorption of  $N_2$  in two hours at  $900^{\circ}$  was the same as with 15 per cent.  $CaCl_2$  at  $800^{\circ}$ . The effect of the quantity of catalyst added is peculiar. With increasing quantities of  $CaCl_2$  the  $N_2$ -absorption in two hours increases rapidly at first, and then more slowly, until with 30 per cent.  $CaCl_2$  almost complete azotisation is obtained. With  $CaF_2$  the  $N_2$ -absorption in two hours rises rapidly to a maximum with increasing percentage of  $CaF_2$ , and then falls on further addition. At  $800^{\circ}$  the maximum absorption in two hours (8 per cent.  $N_2$ ) is obtained with 5 per cent.  $CaF_2$ , and at  $900^{\circ}$  with 3 per cent.  $CaF_2$  (29 per cent.  $N_2$ ). The behaviour of  $CaC_2$  alone, compared with that of a mixture with  $CaCl_2$  or  $CaF_2$ , seems to show that the influence of the addition is to remove some resistance to the continued  $N_2$ -absorption.

Foerster and Jacoby assume that the resistance is due to protecting layers of reaction products on the carbide, and that the liquefaction or softening of a portion of the reaction-mass by the  $\text{CaCl}_2$ , the melting-point of which is below  $800^\circ$ , prevents the existence of these protecting layers, and explains its favourable action. The difference in the behaviour of pure and technical  $\text{CaC}_2$  is similarly explained by the presence of  $\text{CaO}$  in the latter. This is known to lower the melting-point of  $\text{CaC}_2$ , and an incipient softening of the mass at  $1100^\circ$  might well explain the absorption of nitrogen by technical carbide. It also explains why further addition of  $\text{CaO}$  has no considerable effect, and why the addition of substances which only increase the porosity of the mass, but which cannot effect liquefaction, do not help absorption. Besides dissolving protecting layers, liquefaction of the mass allows nitrogen to dissolve, and thus increases the velocity of its action. These results might be considered of importance technically, as the lower reaction-temperature caused by salt additions means a saving of fuel and less wear of the reaction-chambers. It is maintained, however, from the technical side,<sup>146</sup> that even though the temperature of active absorption is lowered by these salts, this is not of much importance technically, as with large masses the great heat liberated by the reaction would raise the temperature to that usually employed without additions.

In a later investigation Foerster and Jacoby<sup>133</sup> found that the influence of different quantities of  $\text{CaF}_2$  is practically the same after long heating, and

that even in presence of  $\text{CaF}_2$  at  $800^\circ$ - $860^\circ$  the nitrogen absorption is limited. The limiting value for a given temperature is independent of the percentage of  $\text{CaF}_2$  (up to 10 per cent.), which determines, however, the velocity with which the saturation-point is reached. They assume that at these temperatures the  $\text{CaF}_2$  is unable to remove the whole of the protecting layer from the  $\text{CaC}_2$ .  $\text{CaCl}_2$  has a much greater solvent action, corresponding to its lower melting-point. They agree with Bredig, Fraenkel, and Wilke, however, that the action does not depend on the melting-point of the added salt alone, but on the whole complicated melting-point diagram of the system. They also found that the velocity of nitrogen absorption by  $\text{CaC}_2$ - $\text{CaF}_2$  mixtures was proportional to the pressure.

Pollacci<sup>147</sup> found that  $\text{K}_2\text{CO}_3$  had a marked accelerating effect. The temperature of absorption depends on the percentage of  $\text{K}_2\text{CO}_3$ . At  $900^\circ$  the absorption is a maximum with 4 per cent.  $\text{K}_2\text{CO}_3$ . Pollacci regards the effect of  $\text{K}_2\text{CO}_3$  as purely catalytic and not due to liquefaction phenomena. As regards the influence of pressure, he found that increase of pressure does not lower the temperature of absorption, but increases the velocity of absorption up to 2 atmos. Increase of pressure above this amount makes little difference to the velocity of absorption.

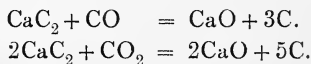
**Technical production of Calcium Cyanamide.**<sup>71, 128, 148</sup>

—Several modifications of the original Frank-Caro process for the manufacture of  $\text{CaCN}_2$  by the action of nitrogen on  $\text{CaC}_2$  have been from time to time pro-

posed. These modifications consisted in the addition to the  $\text{CaC}_2$  of various substances which accelerate the absorption of nitrogen. Of these the most important depend on the addition of  $\text{CaCl}_2$  (Polzenius) or of  $\text{CaF}_2$  (Carlson). The latter does not seem to have been worked technically. The Polzenius method, in which 10 per cent.  $\text{CaCl}_2$  was added to the  $\text{CaC}_2$ , was started at Westeregeln in 1906. In 1908 it came under the control of the Cyanidgesellschaft, which controls the Frank-Caro patents, and was discontinued in 1910, as experience showed that the Frank-Caro process was the more economical.

For a time, owing to the high price of carbide,  $\text{CaCN}_2$  was manufactured from lime, carbon (coal), and nitrogen. The product, however, contained only ca. 12 per cent.  $\text{N}_2$ , compared with ca. 20 per cent. in the product from carbide, and when the price of carbide dropped again a return was made to the original process.

The nitrogen employed must be as free as possible from moisture,  $\text{O}_2$ ,  $\text{CO}$ , and  $\text{CO}_2$ . These act either on the carbide or on the cyanamide, and diminish the percentage of nitrogen in the final product. Thus,  $\text{CO}$  and  $\text{CO}_2$  decompose  $\text{CaC}_2$  as follows:—



Not only do they react with  $\text{CaC}_2$ , but also with  $\text{CaCN}_2$ . The percentage of nitrogen rapidly diminishes when a current of  $\text{CO}$  or  $\text{CO}_2$  is passed over heated  $\text{CaCN}_2$ . In a few factories the nitrogen is prepared by passing air over heated copper turnings, the copper

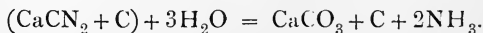


oxide formed being subsequently reduced by heating in a current of reducing gases. More commonly the nitrogen is prepared by the fractional distillation of liquefied air by the Linde or Claude apparatus, which give dry nitrogen containing less than 0.4 per cent. oxygen.

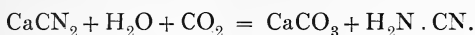
The earlier furnaces were externally heated closed retorts, connected with the nitrogen supply and provided with charging and discharging arrangements. Their great disadvantage was the difficulty of regulating the temperature. The reaction is strongly exothermic, and the temperature rose so high that the walls of the furnace rapidly deteriorated, and the product often set to an extremely hard mass on the furnace walls and could be removed only with difficulty. As at present carried out in the most up-to-date factories, the carbide is finely ground in an air-tight apparatus and filled into drum-shaped retorts, which hold from 300 to 500 kilos. These retorts consist of a sheet-iron cylinder, perforated to allow passage of the nitrogen, and lined externally with refractory material. Down the centre of the retort passes a thin carbon rod, contained in a cardboard tube to separate it from the carbide. The rod is used as a heating resistance. After filling the retort the lid is fixed on air-tight. A number of these retorts are then placed in a long horizontal chamber, the terminals of each carbon rod connected to the current supply, and the chamber closed air-tight. The air is displaced by nitrogen and the current turned on, the connection with the nitrogen supply being maintained. The

nitrogen is admitted at a pressure slightly above atmospheric, so as to prevent access of air. The temperature in the neighbourhood of the resistor rises to about  $1000^{\circ}$ , and the reaction starts from the centre and proceeds outwards. The current is kept on until a certain proportion of the mass has reacted, when the exothermic reaction is able to proceed to completion without further application of heat. The end of the absorption is indicated by a gas-meter on the nitrogen supply. The whole time of absorption is from thirty to forty hours. The drums are then withdrawn and allowed to cool for eight to twelve hours. The black, sintered mass, which occupies a smaller volume than the original carbide, is then removed, ground, treated with water to decompose any unchanged calcium carbide, mixed with a little oil to render it dustless, and packed in sacks. The crude cyanamide contains from 20-22 per cent.  $N_2$ , corresponding to 57-63 per cent.  $CaCN_2$ . It contains in addition about 20 per cent. lime, 7-8 per cent. silica, iron oxide, and alumina, and 14 per cent. carbon in the form of graphite. Various trade names have been given to it—"Kalkstickstoff," "Stickstoffkalk," "lime nitrogen," "nitrogen lime"—but in this country it is usually known as "nitrolim."

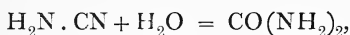
**Uses of Nitrolim.**—The most important property of  $CaCN_2$  is the ease with which it gives up the whole of its nitrogen as ammonia when treated with superheated steam or water under pressure<sup>168</sup>—



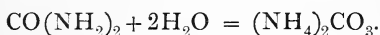
The  $\text{NH}_3$  is absorbed by  $\text{H}_2\text{SO}_4$ , giving pure  $(\text{NH}_4)_2\text{SO}_4$ . The residual  $\text{CaCO}_3 + \text{C}$  may be employed again for the manufacture of  $\text{CaCN}_2$ . When  $\text{CaCN}_2$  is used as a manure it undergoes a complex decomposition, the ultimate products being ammonium compounds. The chief reactions are probably the following. By the action of moisture and  $\text{CO}_2$  in the soil cyanamide is formed—



This is then converted into urea—

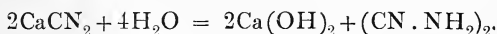


and finally into ammonium carbonate—



Bacteria play an important part in the process. For the advantages and disadvantages of nitrolim as a fertiliser, reference must be made to the numerous articles in the various agricultural journals.

By extracting technical calcium cyanamide with hot water, dicyandiamide is easily obtained pure in crystalline form—

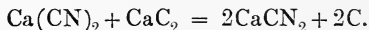


The compound is used in the preparation of organic dyes and as a substitute for ammonium oxalate for lowering the temperature of combustion of explosives. Various other substances, such as urea, guanidine, nitroguanidine, and creatin may

be prepared from calcium cyanamide, and it also forms the basis of "ferrodur," which is used in place of ferrocyanides for the case-hardening and tempering of iron and steel.

Clancy<sup>149</sup> describes a process for the extraction of gold from its ores, in which cyanides are wholly or partly replaced by calcium cyanamide.

**Cyanides from Nitrolim.**<sup>128, 148</sup>—The theory of the transformation of cyanamide to cyanide has already been discussed (p. 98). In practice the crude ( $\text{CaCN}_2 + \text{C}$ ) mixture is fused with common salt, when 90-95 per cent. of the cyanamide is converted into cyanide. The product contains about 30 per cent.  $\text{NaCN}$  and can be used directly for gold extraction, or it may be converted into pure cyanide by decomposing it with acids and absorbing the liberated  $\text{HCN}$  by caustic alkalies. The formation of cyanide from cyanamide is a reversible reaction, and special provision has to be made to prevent re-formation of cyanamide after complete fusion. Further, at the temperature of fusion there may be a decomposition of  $\text{CaCN}_2$  giving  $\text{CaC}_2$ , which can act on cyanide as follows:—



By using appropriate appliances for melting and cooling the materials, these difficulties have been overcome and the conversion of cyanamide into cyanide is practically quantitative.

Factories for the manufacture of cyanamide are in operation in France, Germany, Norway, Italy, Hungary, Switzerland, the United States, and

Japan.<sup>153</sup> No process of any kind for the fixation of atmospheric nitrogen is as yet running in Britain, but large works are in course of erection by Messrs Brunner, Mond & Co. for the manufacture of synthetic ammonia by the direct process.



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